

## Chapter 3

# Vegetable Oils and Animal Fats

### 3.1 Use of Vegetable Oils and Animal Fats in Fuel Engines

Vegetable oils have become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources. More than 100 years ago, Rudolph Diesel tested vegetable oil as the fuel for his engine (Shay, 1993). Vegetable oils have the potential to replace a fraction of the petroleum distillates and petroleum-based petrochemicals in the near future. Vegetable-oil fuels presently do not compete with petroleum-based fuels because they are more expensive. However, with recent increases in petroleum prices and uncertainties surrounding petroleum availability, there is renewed interest in using vegetable oils in diesel engines. The diesel boiling range is of particular interest because it has been shown to reduce particulate emissions significantly relative to petroleum diesel fuel (Giannelos *et al.*, 2002).

Chemically speaking, vegetable oils and animal fats are triglyceride molecules in which three fatty acid groups are esters attached to one glycerol molecule (Gunstone and Hamilton, 2001). Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdoms that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides (Sonntag, 1979).

Chemically, fats and oils are carboxylic esters derived from the single alcohol glycerine and are known as triglycerides. Triglycerides derive from many different carboxylic acids. Triglyceride molecules differ in the nature of the alkyl chain bound to glycerol. The proportions of the various acids vary from fat to fat; each fat has its characteristic composition. Although thought of as esters of glycerine and a varying blend of fatty acids, in fact these oils contain free fatty acids and diglycerides as well. Triglyceride vegetable oils and fats include not only edible but also inedible vegetable oils and fats such as linseed oil, castor oil, and tung oil, used in lubricants, paints, cosmetics, pharmaceuticals, and other industrial purposes.

More than 350 oil-bearing crops have been identified, of which only soybean, palm, sunflower, safflower, cottonseed, rapeseed, and peanut oils are considered

**Table 3.1** Oil species for biofuel production

Group	Source of oil
Major oils	Coconut (Copra), corn (maize), cottonseed, canola (a variety of rapeseed), olive, peanut (groundnut), safflower, sesame, soybean, and sunflower
Nut oils	Almond, cashew, hazelnut, macadamia, pecan, pistachio and walnut
Other edible oils	Amaranth, apricot, argan, artichoke, avocado, babassu, bay laurel, beech nut, ben, Borneo tallow nut, carob pod (algaroba), cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lallemantia, lemon seed, macauba fruit ( <i>Acrocomia sclerocarpa</i> ), meadowfoam seed, mustard, okra seed (hibiscus seed), perilla seed, pequi, ( <i>Caryocar brasiliensis</i> seed), pine nut, poppyseed, prune kernel, quinoa, ramtil ( <i>Guizotia abyssinica</i> seed or Niger pea), rice bran, tallow, tea (camellia), thistle ( <i>Silybum marianum</i> seed), and wheat germ
Inedible oils	Algae, babassu tree, copaiba, honge, jatrophia or ratanjyote, jojoba, karanja or honge, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk cotton tree, and tall
Other oils	Castor, radish, and tung

**Table 3.2** World vegetable and marine oil consumption (million metric ton)

Oil	1998	1999	2000	2001	2002	2003
Soybean	23.5	24.5	26.0	26.6	27.2	27.9
Palm	18.5	21.2	23.5	24.8	26.3	27.8
Rapeseed	12.5	13.3	13.1	12.8	12.5	12.1
Sunflower seed	9.2	9.5	8.6	8.4	8.2	8.0
Peanut	4.5	4.3	4.2	4.7	5.3	5.8
Cottonseed	3.7	3.7	3.6	4.0	4.4	4.9
Coconut	3.2	3.2	3.3	3.5	3.7	3.9
Palm kernel	2.3	2.6	2.7	3.1	3.5	3.7
Olive	2.2	2.4	2.5	2.6	2.7	2.8
Fish	1.2	1.2	1.2	1.3	1.3	1.4
Total	80.7	85.7	88.4	91.8	95.1	98.3

potential alternative fuels for diesel engines (Goering *et al.*, 1982; Pryor *et al.*, 1982). Table 3.1 shows the oil species that can be used in biodiesel production. Worldwide consumption of Soybean oil was the highest in 2003 (27.9 million metric tons). Table 3.2 shows the world vegetable and marine oil consumption between 1998 and 2003.

Vegetable oils are a renewable and potentially inexhaustible source of energy with energy content close to diesel fuel. On the other hand, extensive use of vegetable oils may cause other significant problems such as starvation in developing countries.

Vegetable-oil fuels have not been acceptable because they are more expensive than petroleum fuels. However, with recent increases in petroleum prices and uncertainties surrounding petroleum availability, vegetable oils have become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources (Demirbas, 2003b; Giannelos *et al.*, 2002).

The first use of vegetable oils as a fuel was in 1900. The advantages of vegetable oils as diesel fuel are liquidity, ready availability, renewability, lower sulfur and aromatic content, and biodegradability (Goering *et al.*, 1982). The main disadvantages of vegetable oils as diesel fuel are higher viscosity, lower volatility, and the reactivity of unsaturated hydrocarbon chains. The problems met in long-term engine tests, according to results obtained by earlier researchers (Komers *et al.*, 2001; Darnoko and Cheryan, 2000), may be classified as follows: coking on injectors, more carbon deposits, oil ring sticking, and thickening and gelling of the engine lubricant oil. All vegetable oils are extremely viscous, with viscosities ranging from 10 to 17 times greater than D2 fuel (D2 fuel is a diesel engine fuel with 10 to 20 carbon number hydrocarbons) (Srivastava and Prasad, 2000).

A variety of biolipids can be used to produce biodiesel. These are (a) virgin vegetable oil feedstock; rapeseed and soybean oils are most commonly used, though other crops such as mustard, palm oil, sunflower, hemp, and even algae show promise; (b) waste vegetable oil; (c) animal fats including tallow, lard, and yellow grease; and (d) non-edible oils such as jatropha oil, neem oil, mahua oil, castor oil, tall oil, *etc.*

Soybeans are commonly used in the United States for food products, which has led to soybean biodiesel's becoming the primary source for biodiesel in that country. In Malaysia and Indonesia palm oil is used as a significant biodiesel source. In Europe, rapeseed is the most common base oil used in biodiesel production. In India and southeast Asia, the jatropha tree is used as a significant fuel source.

Algae can grow practically anywhere there is enough sunlight. Some algae can grow in saline water. The most significant difference of algal oil is in the yield and, hence, its biodiesel yield. According to some estimates, the yield (per acre) of oil from algae is over 200 times the yield from the best-performing plant/vegetable oils (Sheehan *et al.*, 1998). Microalgae are the fastest growing photosynthesizing organisms. They can complete an entire growing cycle every few days. Approximately 46 tons of oil/hectare/year can be produced from diatom algae. Different algae species produce different amounts of oil. Some algae produce up to 50% oil by weight. The production of algae to harvest oil for biodiesel has not been undertaken on a commercial scale, but working feasibility studies have been conducted to arrive at the above number.

Specially bred mustard varieties can produce reasonably high oil yields and have the added benefit that the meal left over after the oil has been pressed out can act as an effective and biodegradable pesticide.

## 3.2 Vegetable Oil Resources

World annual petroleum consumption and vegetable oil production is about 4.018 and 0.107 billion tons, respectively. Global vegetable oil production increased from 56 million tons in 1990 to 88 million tons in 2000, following a below-normal

increase. World vegetable and marine oil consumption is tabulated in Table 3.2. Figure 3.1 shows the plots of percentages of world oil consumption by year. Figure 3.2 shows the total global production and consumption of vegetable oil by year. Leading the gains in vegetable oil production was a recovery in world palm oil output, from 18.5 million tons in 1998 to 27.8 million in 2003.

The major exporters of vegetable oils are Malaysia, Argentina, Indonesia, the Philippines, and Brazil. The major importers of vegetable oils are China, Pakistan, Italy, and the United Kingdom. A few countries such as the Netherlands, Germany, the United States, and Singapore are both major exporters as well as importers of vegetable oils (Bala, 2005).

Global vegetable oil consumption rose modestly from 79.5 million tons in 1998 to 96.9 million in 2003. A large portion of the gain occurred in India, where even small price shifts can cause a substantial change in consumption. Indian palm oil

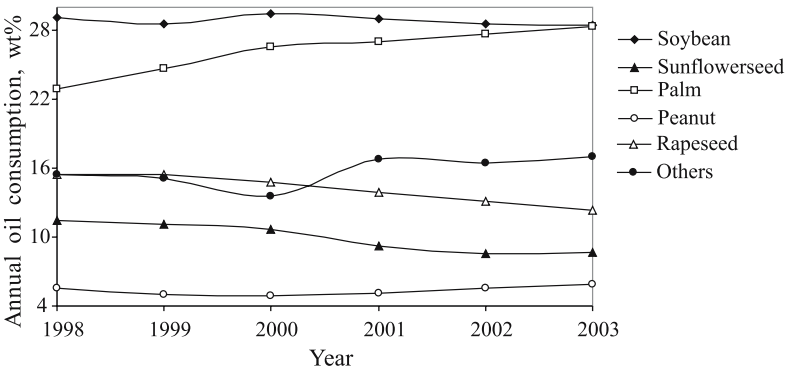


Fig. 3.1 Percentage of world oil consumption by year

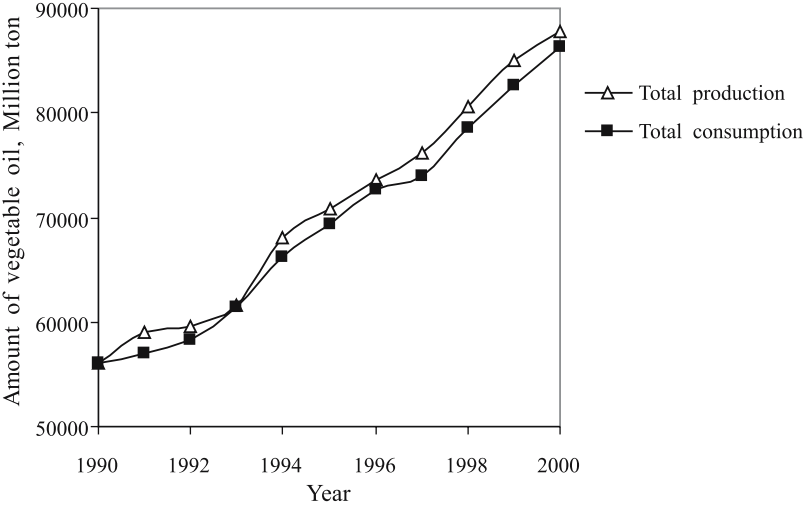


Fig. 3.2 Total global production and consumption of vegetable oil by year

**Table 3.3** Oil and fat feedstock distribution top ten developed countries with self-sufficiency potential in 2006

Feedstock	%
Animal fats	52
Soybean oil	20
Rapeseed oil	11
Palm oil	6
Sunflower oil	5
Other vegetable oils	5

imports climbed to a record 2.5 million tons. Similarly, Pakistan, Iran, Egypt, and Bangladesh sharply increased their vegetable oil imports. In 1999, Pakistan reacted to falling vegetable oil prices with a series of increases that doubled the import duties on soybean oil and palm oil while eliminating duties on oilseeds. Pakistan also raised the import duty on soybean meal from 10% to 35% to stem the influx of Indian exports (Erickson *et al.*, 1980).

Table 3.3 shows the oil and fat feedstock distribution of the top ten developed countries with self-sufficiency potential in 2006.

### 3.2.1 Inedible Oil Resources

The non-edible oils such as jatropha, microalgae, neem, karanja, rubber seed, mahua, silk cotton tree, *etc.* are easily available in developing countries and are very economical comparable to edible oils.

The oils from neem (*Azadirachta indica*) and rubber (*Hevea brasiliensis*) have high free fatty acid (FFA) content. FFAs easily react with alkaline catalysts to form soap that prohibits the separation of biodiesel and glycerol. The soaps of FFAs also cause foaming in aqueous media. The resulting soaps also cause an increase in viscosity, formation of gels, and foams and make the separation of glycerol difficult (Wright *et al.*, 1944; Ma and Hanna, 1999; Demirbas, 2003a).

Vegetable oils have chemical structures different than that of petroleum-based diesel fuels. Vegetable oils containing up to three fatty acids linked to a glycerine molecule with ester linkages are called triglycerides. The fatty acids are characterized by their carbon chain length and in numbers of double bonds. There is little difference between the gross heat content among any of the vegetable oils. Their heat contents were *ca.* 88% of that of D2 fuel (Demirbas, 1998).

Vegetable oils have the potential to substitute a fraction of petroleum-based engine fuels in the near future (Demirbas, 2003b). Possible acceptable processes for converting vegetable oils into reusable products such as gasoline and diesel fuel are solvent extraction, cracking, and pyrolysis (Nagai and Seko, 2000; Bhatia *et al.*, 2003). Vegetable oil fuels are not cost competitive with petroleum-based fuels. Diesel boiling range material from plant oils is of particular interest because

it has been shown to significantly reduce particulate emissions relative to petroleum diesel fuel (Giannalos *et al.*, 2002).

The advantages of biodiesel as diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content (Ma and Hanna, 1999; Knothe *et al.*, 2006), higher cetane number, and higher biodegradability (Mudge and Pereira, 1999; Speidal *et al.*, 2000; Zhang *et al.*, 2003). The main advantages of biodiesel given in the literature include its domestic origin, which would reduce dependency on imported petroleum, high flash point, and inherent lubricity in the neat form (Mittelbach and Remschmidt, 2004; Knothe *et al.*, 2005).

The major disadvantages of biodiesel are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide (NO<sub>x</sub>) emission rates, lower engine speed and power, injector coking, engine compatibility, high price, and higher engine wear.

Biodiesel has higher cloud point and pour point compared to conventional diesel (Prakash, 1998). Neat biodiesel and biodiesel blends increase nitrogen oxide (NO<sub>x</sub>) emissions compared with petroleum-based diesel fuel used in an unmodified diesel engine (EPA, 2002). Peak torque is less for biodiesel than petroleum diesel but occurs at lower engine speed, and generally the torque curves are flatter. Biodiesels on average decrease power by 5% compared to diesel at rated load (Demirbas, 2006).

The main commodity sources for biodiesel production from non-edible oils are plant species such as jatropa or ratanjyote or seemaikattamankku (*Jatropha curcas*), karanja or honge (*Pongamia pinnata*), nagchampa (*Calophyllum inophyllum*), rubber seed tree (*Hevea brasiliensis*), neem (*Azadirachta indica*), mahua (*Madhuca indica* and *Madhuca longifolia*), silk cotton tree (*Ceiba pentandra*), jojoba (*Simmondsia chinensis*), babassu tree, *Euphorbia tirucalli*, microalgae, *etc.* They are easily available in many parts of the world and are very cheap compared to edible oils in India (Karmee and Chadha, 2005).

Two major species of the genus, *Madhuca indica* and *Madhuca longifolia*, are found in India. The oil of the rubber seed tree (*Hevea brasiliensis*) is a non-edible source of biodiesel production. It is found mainly in Indonesia, Malaysia, Liberia, India, Srilanka, Sarawak, and Thailand. Rubber seed kernels (50 to 60% of seed) contain 40 to 50% of brown oil (Ramadhas *et al.*, 2004). Two major species of the genus, the oil palms *Elaeis guineensis* and *Elaeis oleifera*, are in Africa and Central/South America, respectively. Among vegetable oils, the price of palm oil is cheapest in palm-producing countries such as Malaysia, Indonesia, Thailand, and Korea. Neem oil is a vegetable oil pressed from the fruits and seeds of Neem (*Azadirachta indica*), an evergreen tree that is endemic to the Indian subcontinent and has been introduced to many other areas native to India and Burma, growing in tropical and semitropical regions. Jojoba oil is produced in the seed of the jojoba (*Simmondsia chinensis*) plant, a shrub native to southern Arizona, southern California, and northwestern Mexico (Wikipedia, 2007). The oil of the silk cotton tree (*Ceiba pentandra*) is a non-edible source of biodiesel production. The tree belongs to the family *Bornbacacea*. The silk cotton tree has great economic

importance for both domestic and industrial uses in Nigeria. The seeds are also used as food/feed for humans and livestock in many parts of the world such as India, Tanzania, and Mozambique. *Ceiba pentandra* crude oil was extracted for 24 hours using a Soxhlet extractor with n-hexane as a solvent (Das *et al.*, 2002). Babassu tree is a species of palm tree that is a source of light yellow clear oil. There are both edible and non-edible species of babassu oils. A non-edible species of the oil is obtained from the babassu tree, which is widely grown in Brazil. The viscosity at 313.2 K and the Cetane number values of babassu oil are 3.6 cSt and 63, respectively (Srivastava and Prasad, 2000).

Fatty acid profiles of seed oils of 75 plant species having 30% or more fixed oil in their seed/kernel were examined, and *Azadirachta indica*, *Calophyllum inophyllum*, *Jatropha curcas*, and *Pongamia pinnata* were found most suitable for use as biodiesel (Azam *et al.*, 2005). The seed oil of *Jatropha* was used as a diesel fuel substitute during World War II and as blends with diesel (Foidl *et al.*, 1996; Gubitz *et al.*, 1999). Thus *Jatropha curcas* and *Pongamia pinnata* (Karanja) are most suitable for the purpose of producing renewable fuel as biodiesel (Meher *et al.*, 2006a; Meher *et al.*, 2006b). *Jatropha* and Karanja have high oil content (25% to 30%) (Foidl *et al.*, 1996).

From 1978 to 1996, the U.S. Department of Energy's Office of Fuels Development funded a program to develop renewable transportation fuels from algae (Sheehan *et al.*, 1998). Most current research on oil extraction is focused on microalgae to produce biodiesel from algal oil. Algal oil processes into biodiesel as easily as oil derived from land-based crops. The lipid and fatty acid contents of microalgae vary in accordance with culture conditions. All algae contain proteins, carbohydrates, lipids, and nucleic acids in varying proportions. Algal oil contains saturated and monounsaturated fatty acids. The fatty acids were determined in the algal oil in the following proportions: 36% oleic (18:1), 15% palmitic (16:0), 11% stearic (18:0), 8.4% iso-17:0, and 7.4% linoleic (18:2). The high proportion of saturated and monounsaturated fatty acids in this alga is considered optimal from a fuel quality standpoint in that fuel polymerization during combustion would be substantially less than what would occur with polyunsaturated fatty-acid-derived fuel (Sheehan *et al.*, 1998).

Oil from algae, bacteria, and fungi have also been investigated (Shay, 1993). Microalgae have been examined as a source of methyl ester diesel fuel (Nagel and Lemke, 1990), and terpenes and latexes also were studied as diesel fuels (Calvin, 1985).

Algae can grow virtually anywhere with enough sunshine. Some algae can grow in saline water. The most significant distinguishing characteristic of algal oil is in the yield and hence its biodiesel yield. According to some estimates, the yield (per acre) of oil from algae is over 200 times the yield from the best-performing plant/vegetable oils (Sheehan *et al.*, 1998). Microalgae are the fastest growing photosynthesizing organisms. They can complete an entire growing cycle every few days. Approximately 46 tons of oil/hectare/year can be produced from diatom algae. Different algae species produce different amounts of oil. Some algae produce up to 50% oil by weight. Microalgae have much faster growth rates than

terrestrial crops. The per unit area yield of oil from algae is estimated to be between 5,000 and 20,000 gallons per acre per year, which is 7 to 31 times greater than the next best crop, palm oil.

### 3.3 Vegetable Oil Processing

Vegetable oil processing involves the extraction and processing of oils and fats from vegetable and animal resources. The oils and fats are extracted from a variety of fruits, seeds, and nuts. Natural vegetable oils and animal fats are extracted or pressed to obtain crude oil or fat. These usually contain free fatty acids, phospholipids, sterols, water, odorants, and other impurities. Even refined oils and fats contain small amounts of free fatty acids and water (Ma and Hana, 1999).

The preparation of raw materials includes husking, cleaning, crushing, and conditioning. The extraction processes are generally mechanical (boiling for fruits, pressing for seeds and nuts) or involve the use of solvent such as hexane. After boiling, the liquid oil is skimmed; after pressing, the oil is filtered; and after solvent extraction, the crude oil is separated and the solvent is evaporated and recovered. Residues are conditioned (*e.g.*, dried) and are reprocessed to yield byproducts such as animal feed. Crude oil refining includes degumming, neutralization, bleaching, deodorization, and further refining (Demirbas and Kara, 2006).

Corn, cottonseed, and peanut oil processing are similar to soybean processing, except for differences in the preparation of soybean for oil extraction. The process for soybeans typically consists of three main steps: oilseed handling/elevator operations, preparation of soybeans for solvent extraction, and oil refining.

Color-producing substances (*i.e.*, carotenoids, chlorophyll) within oil are removed by a bleaching process, which employs the use of adsorbents such as acid-activated clays. Volatile components are removed by deodorization, which uses steam injection under a high vacuum and temperature. The refined oil is then filtered and stored until used or transported.

An important step in vegetable oil purification is physical refining by removing free fatty acids present in the vegetable. This separation is carried out at a low temperature to reduce the degradation of the final products at high vacuum. The free fatty acids can be removed using stripping steam at 525 K at 2 to 3 mm Hg column top pressure.

#### 3.3.1 Recovery of Vegetable Oils from Plants

Vegetable oils are recovered from plants by chemical extraction using solvent extracts. The most common extraction solvent is petroleum-derived hexane. Another method of vegetable oil recovery is physical extraction, which does not use solvent extracts. Supercritical carbon dioxide can also be used for extraction



**Table 3.4** Properties of supercritical fluids

Compound	Boiling point (K)	Critical temperature (K)	Critical pressure (atm)
CH <sub>3</sub> OH	337.9	513.7	78.9
CO <sub>2</sub>	194.7	304.5	72.9
H <sub>2</sub> O	373.2	647.6	226.8
NH <sub>3</sub>	239.8	405.5	111.3
SiF <sub>6</sub>	209.4	318.8	37.1
N <sub>2</sub> O	184.2	309.7	71.4
C <sub>6</sub> H <sub>14</sub>	342.2	507.3	30.5
C <sub>5</sub> H <sub>12</sub>	309.3	469.7	34.1
C <sub>2</sub> H <sub>5</sub> OH	369.2	516.2	64.0

and is non-toxic (Eisenmenger *et al.*, 2005; Rajaei *et al.*, 2005). Supercritical carbon dioxide effectively extracts vegetable oils and fats (Fang *et al.*, 2007).

Supercritical fluid extraction (SFE) can reduce sample preparation time, and recovery using the methods can be equal to or better than that of the classical extraction techniques for solid and semisolid samples (Demirbas, 1991a). SFE is generally carried out in a mechanically stirring or rocking batch reactor at the solvent's critical temperature and pressure (Demirbas, 1991b). SFE is attracting a great deal of interest because the technique can considerably reduce sample preparation time and can provide analyte recovery from solid and semisolid samples that is equal to or better than that of classical extraction techniques such as Soxhlet extraction (Roselius *et al.*, 1985; Paulaitis *et al.*, 1983; Penninger *et al.*, 1985). Examples of pilot plant or commercial applications include decaffeination of coffee, removal of nicotine from tobacco, deasphalting of petroleum, extraction of oil from oilseeds, and extraction of essential oils for flavorings and perfumes (Roselius *et al.*, 1985; Schneider, 1978; Brignole, 1986). Table 3.4 shows the properties of some supercritical fluids.

### 3.3.2 Vegetable Oil Refining

Crude vegetable oils contain trace amounts of naturally occurring materials such as proteinaceous material, free fatty acids, and phosphatides. If physical refining is subsequently employed, it is essential to degum oils that have high phosphatide content for both economic and product quality purposes. The purpose of caustic refining is to remove free fatty acids, phosphatides, and other materials including protein meal, glycerol, carbohydrates, resins, and metals.

Crude vegetable oils obtained by oil seed processes have to be refined to remove undesirable substances. The typical oil refining process includes degumming, chemical or physical refining, bleaching, vintORIZATION, and deodorization. Deodorization is an important step in the oil refining process. During this step, steam at 1 to 6 mm Hg pressure is injected into the oil at 490 to 550 K to eliminate

free fatty acids, aldehydes, unsaturated hydrocarbons, and ketones, which cause undesirable odors and flavors in the oil (Demirbas and Kara, 2006).

The crude vegetable oil quality is very important to obtain high-quality refined oil. The oil should be efficiently degummed to remove phospholipids as well as heavy metals and bleached to remove pigments and metals.

Degummed crude oil is subjected to a further refining process. For this purpose, caustic soda (NaOH) is fed to the oil in the proper quantity to react with the free fatty acids, phosphatides, and the other impurities. Soap stock and other impurities are separated from the oil by centrifuges. Caustic soda is not completely selective in reacting with free fatty acids and phosphatides; therefore, some triglycerides are hydrolyzed and saponified (broken down and converted into soap) (Demirbas and Kara, 2006). In addition, some color reduction is also achieved by pigment removal.

### **3.4 The Use of Vegetable Oils as Diesel Fuel**

The use of vegetable oils in diesel engines is nearly as old as the diesel engine itself. The use of vegetable oils as an alternative renewable fuel was proposed in the early 1980s (Bartholomew, 1981). The most advanced study with sunflower oil occurred in South Africa because of the oil embargo (Ma and Hanna, 1999). The first engine like the diesel engine was developed in the 1800s for fossil fuels. Famous German inventor Rudolph Diesel designed the original diesel engine to run on vegetable oil. Dr. Diesel used peanut oil to fuel one of his engines at the Paris Exposition of 1900 (Nitschke and Wilson, 1965). Because of the high temperatures created, the engine was able to run a variety of vegetable oils including hemp and peanut oil. Life for the diesel engine began in 1893 when Dr. Diesel published a paper entitled "The theory and construction of a rational heat engine". At the 1911 World's Fair in Paris, Dr. Diesel ran his engine on peanut oil and declared "the diesel engine can be fed with vegetable oils and will help considerably in the development of the agriculture of the countries which use it". One of the first uses of transesterified vegetable oil (biodiesel) was powering heavy-duty vehicles in South Africa before World War II (Demirbas, 2002a).

The first International Conference on Plant and Vegetable Oils as Fuels was held in Fargo, North Dakota in August 1982. The primary concerns discussed were the cost of the fuel, the effects of vegetable oil fuels on engine performance and durability, and fuel preparation, specifications, and additives (Ma and Hana, 1999). Oil production, oilseed processing, and extraction also were considered in this meeting (ASAE, 1982).

### 3.4.1 Physical and Chemical Properties of Vegetable Oils

Vegetable oils and fats are substances derived from plants that are composed of triglycerides. Oils extracted from plants have been used in many cultures since ancient times. The oily seed and nut kernels contain 20 to 60% oil. The fatty acid compositions of vegetable oils and fats are listed in Table 3.5.

As can be seen in Table 3.5, palmitic (16:0) and stearic (18:0) are the two most common saturated fatty acids, with every vegetable oil containing at least a small amount of each one. Similarly, oleic (18:1) and linoleic (18:2) were the most common unsaturated fatty acids. Many of the oils also contained some linolenic acid (18:3).

Today, the world's largest producer of soybeans is the USA, with the majority of cultivation located in the midwestern and southern USA. Soybeans must be carefully cleaned, dried, and dehulled prior to oil extraction. There are three main methods for extracting oil from soybeans. These procedures are hydraulic pressing, expeller pressing, and solvent extraction (Erickson *et al.*, 1980). Soybean oil composition is compared to other oils and normal and alternate compositions are shown and considered.

**Table 3.5** Fatty acid compositions of vegetable oils and fats<sup>a</sup>

Sample	16:0	16:1	18:0	18:1	18:2	18:3	Others
Cottonseed	28.7	0	0.9	13.0	57.4	0	0
Poppyseed	12.6	0.1	4.0	22.3	60.2	0.5	0
Rapeseed	3.8	0	2.0	62.2	22.0	9.0	0
Safflowerseed	7.3	0	1.9	13.6	77.2	0	0
Sunflowerseed	6.4	0.1	2.9	17.7	72.9	0	0
Sesameseed	13.1	0	3.9	52.8	30.2	0	0
Linseed	5.1	0.3	2.5	18.9	18.1	55.1	0
Wheat grain <sup>a</sup>	20.6	1.0	1.1	16.6	56.0	2.9	1.8
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Corn marrow	11.8	0	2.0	24.8	61.3	0	0.3
Castor <sup>b</sup>	1.1	0	3.1	4.9	1.3	0	89.6
Tallow	23.3	0.1	19.3	42.4	2.9	0.9	2.9
Soybean	11.9	0.3	4.1	23.2	54.2	6.3	0
Bay laurel leaf <sup>c</sup>	25.9	0.3	3.1	10.8	11.3	17.6	31.0
Peanut kernel <sup>d</sup>	11.4	0	2.4	48.3	32.0	0.9	4.0
Hazelnut kernel	4.9	0.2	2.6	83.6	8.5	0.2	0
Walnut kernel	7.2	0.2	1.9	18.5	56.0	16.2	0
Almond kernel	6.5	0.5	1.4	70.7	20.0	0	0.9
Olive kernel	5.0	0.3	1.6	74.7	17.6	0	0.8
Coconut <sup>e</sup>	7.8	0.1	3.0	4.4	0.8	0	65.7

\* xx:y: xx number of carbon atoms; y number of double bonds

<sup>a</sup> Wheat grain oil contains 11.4% of 8:0 and 0.4% of 14:0 fatty acids

<sup>b</sup> Castor oil contains 89.6% ricinoleic acid

<sup>c</sup> Bay laurel oil contains 26.5% of 12:0 and 4.5% of 14:0 fatty acids

<sup>d</sup> Peanut kernel oil contains about 2.7% of 22:0 and 1.3% of 24:0 fatty acids

<sup>e</sup> Coconut oil contains about 8.9% of 8:0, 6.2% 10:0, 48.8% of 12:0, and 19.9% of 14:0 fatty acids

Diesel fuel can also be replaced by biodiesel made from vegetable oils. Biodiesel is now mainly being produced from soybean and rapeseed oils. Soybean oil is of primary interest as a biodiesel source in the USA, while many European countries use rapeseed oil, and countries with a tropical climate prefer to use coconut oil or palm oil.

Palm oil is widely grown in southeast Asia; 90% of the palm oil produced is used for food and the remaining 10% for non-food consumption, such as the production of oleo-chemicals (Leng *et al.*, 1999). An alternative use could be its conversion to liquid fuels and chemicals. Conversion of palm oil into biodiesel using methanol has been reported (Yarmo *et al.*, 1992). There are great differences between palm oil and palm kernel oil with respect to their physical and chemical characteristics. Palm oil contains mainly palmitic (16:0) and oleic (18:1) acids, the two common fatty acids, and about 50% saturated fat, while palm kernel oil contains mainly lauric acid (12:0) and more than 89% saturated fat (Demirbas, 2003c).

Rapeseed has been grown in Canada since 1936. Hundreds of years ago, Asians and Europeans used rapeseed oil in lamps. Cottonseed oil is used almost entirely as a food material. Sesame, olive, and peanut oils can be used to add flavor to a dish. Walnut oil is high-quality edible oil refined by purely physical means from quality walnuts. Poppy seeds are tiny seeds contained within the bulb of the poppy flower, also known as the opium plant (*Papaver somniferum*). Poppy seed oil is high in linoleic acid (typically 60 to 65%) and oleic acid (typically 18 to 20%) (Bajpai *et al.*, 1999).

Drying oils are vegetable oils that dry to a hard finish at normal room temperature. The polyunsaturated acid (linoleic and linolenic acids) content of a drying oil is high. Such oils are used as the basis of oil paints and in other paint and wood-finishing applications. Walnut, sunflower, safflower, dammar, linseed, poppyseed, stillingia, tang, and vernonia oils are drying oils.

Table 3.6 shows the comparisons of some fuel properties of vegetable oils with D2 fuel. The heat contents of vegetable oils are *ca.* 88% of that of D2. There is little difference between the gross heat content of any of the vegetable oils (Demirbas,

**Table 3.6** Comparisons of some fuel properties of vegetable oils with D2 fuel

	Heating value	Density	Viscosity at 300 K	
Fuel type	(MJ/kg)	(kg/m <sup>3</sup> )	(mm <sup>2</sup> /s)	Cetane number <sup>a</sup>
D2 fuel	43.4	815	4.3	47.0
Sunflower oil	39.5	918	58.5	37.1
Cottonseed oil	39.6	912	50.1	48.1
Soybean oil	39.6	914	65.4	38.0
Corn oil	37.8	915	46.3	37.6
Opium poppy oil	38.9	921	56.1	—
Rapeseed oil	37.6	914	39.2	37.6

<sup>a</sup> Cetane number is a measure of the ignition quality of diesel fuel.

1998). The density values of vegetable oils are between 912 and 921 kg/m<sup>3</sup>, while that of D2 fuel is 815 kg/m<sup>3</sup>. The kinematic viscosity values of vegetable oils vary between 39.2 and 65.4 mm<sup>2</sup>/s at 300 K. The vegetable oils are all extremely viscous, with viscosities ranging from 9 to 15 times greater than D2 fuel (Table 3.6).

Twelve crop (cottonseed, poppyseed, rapeseed, safflowerseed, sunflowerseed, soybean, corn marrow, sesameseed, linseed, castor, wheat grain, and bay laurel leaf) and five kernel (peanut, hazelnut, walnut, almond, and olive) samples used in this study were supplied from different Turkish agricultural sources. Physical analyses of the samples were carried out according to the standard test methods: ASTM D445, ASTM D613, and ASTM D524 for kinematic viscosity (KV), cetane number (CN), and carbon residue (CR), respectively. However, as too low amounts of wheat grain, bay laurel leaf, and corn marrow oils were available for determination of cetane number using the standard method, a calculated cetane number was established according to Goering *et al.* (1982). Chemical analyses of the samples were carried out according to the standard test methods: ASTM D 2015-85, ASTM D5453-93, ASTM D482-91, AOCs CD1-25, and AOCs CD3 for higher heating value (HHV), sulfur content, ash content, iodine value, and saponification value, respectively. The other standard test methods for fuel properties are presented in Table 3.7. Fatty acid compositions of oil samples were determined by gas chromatographic (GC) analysis. The oil samples were saponified for 3.5 h and 338 K with 0.5 N methanolic KOH to liberate the fatty acids present as their esters. After acidification of the saponified solutions with 1.5 N HCl acid, acids were then weighed and methylated with diazomethane according to the method of Schelenk and Gellerman (1960). The methyl esters of the fatty acids were analyzed by GC (Hewlett-Packard 5790) on a 12 m long and 0.2 mm inside diameter capillary column coated with Carbowax PEG 20. The detector was a FID. Helium was used as carrier gas. The flame ionization detector temperature was 500 K.

The oven temperature was kept at 450 K for 25 min. After that, the oven was heated with a heat ratio of 5 K/min to 495 K. Spectra of methyl esters were recorded

**Table 3.7** Determination of physical and chemical properties using standard test methods

Property	Symbol	Standard method	Unit
Density	d	ASTM D4052-91	g/ml
Iodine value	IV	AOCs CD1-25 1993	centigram I/g oil
Saponification value	SV	AOCs CD3 1993	mg KOH/g oil
Higher heating value	HHV	ASTM D2015-85	MJ/kg
Cloud point	CP	ASTM D2500-91	K
Pour point	PP	ASTM D97-93	K
Flash point	FP	ASTM D93-94	K
Cetane number	CN	ASTM D613	—
Kinematic viscosity	KV	ASTM D445	mm <sup>2</sup> /s at 311 K
Sulfur content	SC	ASTM D5453-93	wt. %
Carbon residue	CR	ASTM D 524	wt. %
Ash content	AC	ASTM D482-91	wt. %

**Table 3.8** Physical and chemical properties of oil samples

Vegetable oil	KV	CR	CN	HHV	AC	SC	IV	SV
Cottonseed	33.7	0.25	33.7	39.4	0.02	0.01	113.20	207.71
Poppyseed	42.4	0.25	36.7	39.6	0.02	0.01	116.83	196.82
Rapeseed	37.3	0.31	37.5	39.7	0.006	0.01	108.05	197.07
Safflowerseed	31.6	0.26	42.0	39.5	0.007	0.01	139.83	190.23
Sunflowerseed	34.4	0.28	36.7	39.6	0.01	0.01	132.32	191.70
Sesameseed	36.0	0.25	40.4	39.4	0.002	0.01	91.76	210.34
Linseed	28.0	0.24	27.6	39.3	0.01	0.01	156.74	188.71
Wheat grain	32.6	0.23	35.2	39.3	0.02	0.02	120.96	205.68
Corn marrow	35.1	0.22	37.5	39.6	0.01	0.01	119.41	194.14
Castor	29.7	0.21	42.3	37.4	0.01	0.01	88.72	202.71
Soybean	33.1	0.24	38.1	39.6	0.006	0.01	69.82	220.78
Bay laurel leaf	23.2	0.20	33.6	39.3	0.03	0.02	105.15	220.62
Peanut kernel	40.0	0.22	34.6	39.5	0.02	0.01	119.55	199.80
Hazelnut kernel	24.0	0.21	52.9	39.8	0.01	0.02	98.62	197.63
Walnut kernel	36.8	0.24	33.6	39.6	0.02	0.02	135.24	190.82
Almond kernel	34.2	0.22	34.5	39.8	0.01	0.01	102.35	197.56
Olive kernel	29.4	0.23	49.3	39.7	0.008	0.02	100.16	196.83

with a VG 70-250-SE mass spectrometer with double focusing. Ionization was carried out at 70 eV. The mass spectrometer was fitted to the gas chromatograph by means of a capillary glass jet separator.

Table 3.8 lists the physical and chemical properties of the oil samples. Viscosity values (KV) of the oil samples range from 23.2 to 42.4 mm<sup>2</sup>/s at 311 K. The vegetable oils are all extremely viscous, with viscosities ranging from 10 to 20 times that of the ASTM upper limit given for diesel fuels (2.7 mm<sup>2</sup>/s).

Higher heating values (HHVs) of the oil samples range from 39.3 to 39.8 MJ/kg. Castor oil has an exceptional HHV (37.4 MJ/kg). The oxygen content of castor oil is higher than that of vegetable oils due to the ricinoleic acid in its structure. Ricinoleic acid is the only 18:1 fatty acid that contains a hydroxyl group. Because castor oil contains a hydroxyl group, its HHV is lower than the others.

The cetane numbers of the oil samples range from 27.6 to 52.9. The iodine values (IVs) and saponification values (SVs) of the oil samples range from 69.82 to 156.74 and from 188.71 to 220.78, respectively.

The SV of an oil decreases with increase of its molecular weight. The percentages of C and H in an oil decrease with an increase in molecular weight. The increase in SV results in a decrease in the heat content of an oil. The increase in IV (*i.e.*, carbon-carbon double bond,  $\text{--C=C--}$ , content of oil) results in a decrease in the heat content of an oil. The heat content of the oil depends on the SV and IV. Therefore, for calculation of the HHVs (MJ/kg) of oil samples, Eq. (3.1) was proposed (Demirbas, 1998).

$$\text{HHV} = 49.43 - 0.041 (\text{SV}) - 0.015 (\text{IV}) \quad (3.1)$$

Thus the heating values of the vegetable oils can be calculated using their SVs and IVs obtained non-calorimetrically from simple chemical analyses.

The carbon residue (CR), sulfur content (SC), and ash content (AC) of the oil samples range from 0.20 to 0.31 wt.%, from 0.01 to 0.02 wt.%, and from 0.002 to 0.02 wt.%, respectively (Table 3.8).

The increase in heat content results from a high increase in the number of carbons and hydrogens, as well as an increase in the ratio of these elements relative to oxygen. A decrease in heat content is the result of fewer hydrogen atoms (*i.e.*, greater unsaturation) in the fuel molecule. An examination of data obtained for a great many compounds has shown that the HHV of an aliphatic hydrocarbon agrees rather closely with that calculated by assuming a certain characteristic contribution from each structural unit (Morrison and Boyd, 1983). For open-chain alkanes, each methylene group,  $-\text{CH}_2-$ , contributes very close to 46,956 kJ/kg.

### 3.4.2 Direct Use of Vegetable Oils in Diesel Engines

The use of vegetable oils as an alternative renewable fuel competing with petroleum was proposed in the early 1980s. The advantages of vegetable oils as diesel fuel are as follows (Demirbas, 2003b):

- Portability
- Ready availability
- Renewability
- Higher heat content (about 88% of D2 fuel)
- Lower sulfur content
- Lower aromatic content
- Biodegradability

Full combustion of a fuel requires in existence the amount of stoichiometric oxygen. However, the amount of stoichiometric oxygen generally is not enough for full combustion because the fuel is not oxygenated. The structural oxygen content of fuel increases the combustion efficiency of the fuel due to increased mixing of oxygen with the fuel during combustion. For these reasons, the combustion efficiency and cetane number of vegetable oil are higher than those of diesel fuel, and the combustion efficiency of methanol and ethanol is higher than that of gasoline.

The disadvantages of vegetable oils as diesel fuel are (Pryde, 1983):

- Higher viscosity
- Lower volatility
- The reactivity of unsaturated hydrocarbon chains

Problems appear only after the engine has been operating on vegetable oils for longer periods of time, especially with direct-injection engines. The problems

include (a) coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices, (b) carbon deposits, (c) oil ring sticking, and (d) thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils (Ma and Hana, 1999).

Among the renewable resources for the production of alternative fuels, triglycerides have attracted much attention as alternative diesel engine fuels (Shay, 1993). However, the direct use of vegetable oils and/or oil blends is generally considered to be unsatisfactory and impractical for both direct injection and indirect type diesel engines because of their high viscosities and low volatilities, injector coking and trumpet formation on the injectors, higher level of carbon deposits, oil ring sticking, and thickening and gelling of the engine lubricant oil, acid composition (the reactivity of unsaturated hydrocarbon chains), and free fatty acid content (Ma and Hanna, 1999; Darnoko and Cheryan, 2000; Srivastava and Prasad, 2000; Komers *et al.* 2001). Consequently, different methods have been considered to reduce the viscosity of vegetable oils such as dilution, microemulsification, pyrolysis, catalytic cracking, and transesterification. Methods based on pyrolysis (Alencar *et al.* 1983; Dykstra *et al.*, 1988; Agra *et al.*, 1992; Adjaye *et al.*, 1995, 1996; Shay, 1993; Dandik and Aksoy, 1998; Bhatia *et al.*, 1999; Lima *et al.*, 2004) and microemulsification (Billaud *et al.*, 1995) have been studied but are not entirely satisfactory.

Vegetable oils can be used as fuels for diesel engines, but their viscosities are much higher than that of common diesel fuel and require modifications of the engines (Kerschbaum and Rinke, 2004). Vegetable oils could only replace a very small fraction of transport fuel. Different methods of reducing the high viscosity of vegetable oils have been considered:

1. Dilution of 25 parts of vegetable oil with 75 parts of diesel fuel
2. Microemulsions with short-chain alcohols such as ethanol or methanol
3. Transesterification with ethanol or methanol, which produces biodiesel
4. Pyrolysis and catalytic cracking, which produces alkanes, cycloalkanes, alkenes, and alkylbenzenes.

#### **3.4.2.1 Dilution of Oils**

Dilution of oils with solvents and microemulsions of vegetable oils lowers the viscosity and mitigates some engine performance problems such as injector coking and carbon deposits, *etc.* To dilute vegetable oils the addition of 4% ethanol to the oils increases the brake thermal efficiency, brake torque, and brake power while decreasing brake-specific fuel consumption. Since the boiling point of ethanol is less than that of vegetable oils, it could assist in the development of the combustion process through an unburned blend spray (Bilgin *et al.*, 2002).

The viscosity of oil can be lowered by blending with pure ethanol. Twenty-five parts of sunflower oil and 75 parts of diesel were blended as diesel fuel (Ziejewski



*et al.*, 1986). The viscosity was 4.88 cSt at 313 K, while the maximum specified ASTM value was 4.0cSt at 313 K. This mixture was not suitable for long-term use in a direct injection engine. Another study was conducted using the dilution technique on the same frying oil (Karaosmonoglu, 1999).

The addition of 4% ethanol to D2 fuel increases the brake thermal efficiency, brake torque, and brake power while decreasing brake-specific fuel consumption. Since the boiling point of ethanol is less than that of D2 fuel, it could assist the development of the combustion process through an unburned blend spray (Bilgin *et al.*, 2002).

### 3.4.2.2 Microemulsion of Oils

To reduce the high viscosity of vegetable oils, microemulsions with immiscible liquids such as methanol and ethanol and ionic or non-ionic amphiphiles have been studied (Billaud *et al.*, 1995). The short engine performances of both ionic and non-ionic microemulsions of ethanol in soybean oil were nearly as good as that of D2 fuel (Goering *et al.*, 1982).

To solve the problem of the high viscosity of vegetable oils, microemulsions with solvents such as methanol, ethanol, and 1-butanol have been studied. All microemulsions with butanol, hexanol, and octanol met the maximum viscosity requirement for D2 fuel. The 2-octanol was found to be an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil (Schwab *et al.*, 1987; Ma and Hanna, 1999).

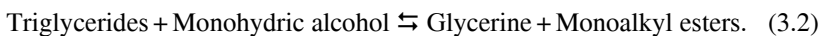
Ziejewski *et al.* (1984) prepared an emulsion of 53% (vol) alkali-refined and winterized sunflower oil, 13.3% (vol) 190-proof ethanol, and 33.4% (vol) 1-butanol. This non-ionic emulsion had a viscosity of 6.31 cSt at 313 K, a cetane number of 25, and an ash content of less than 0.01%. Lower viscosities and better spray patterns (more even) were observed with an increase of 1-butanol. In a 200-h laboratory screening endurance test, no significant deteriorations in performance were observed, but irregular injector needle sticking, heavy carbon deposits, incomplete combustion, and an increase in lubricating oil viscosity were reported (Ma and Hanna, 1999).

A microemulsion prepared by blending soybean oil, methanol, 2-octanol, and cetane improver in the ratio of 52.7:13.3:33.3:1.0 also passed the 200-h EMA test (Goering, 1984). Schwab *et al.* (1987) used the ternary phase equilibrium diagram and the plot of viscosity versus solvent fraction to determine the emulsified fuel formulations. All microemulsions with butanol, hexanol, and octanol met the maximum viscosity requirement for D2. The 2-octanol was an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil. Methanol was often used due to economic advantage over ethanol.

### 3.4.2.3 Transesterification of Oils and Fats

Among all these alternatives, transesterification seems to be the best choice as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel and the process is relatively simple. In the esterification of an acid, an alcohol acts as a nucleophilic reagent; in the hydrolysis of an ester, an alcohol is displaced by a nucleophilic reagent. This alcoholysis (cleavage by an alcohol) of an ester is called transesterification (Gunstone and Hamilton, 2001).

Transesterified vegetable oils have proven to be a viable alternative diesel engine fuel with characteristics similar to those of diesel fuel. The transesterification reaction proceeds with catalyst or any unused catalyst by using primary or secondary monohydric aliphatic alcohols having between one and eight carbon atoms as follows:



Transesterification is catalyzed by a base (usually alkoxide ion) or acid ( $\text{H}_2\text{SO}_4$  or dry  $\text{HCl}$ ). The transesterification is an equilibrium reaction. To shift the equilibrium to the right, it is necessary to use a large excess of the alcohol or else to remove one of the products from the reaction mixture. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation. Although short-term tests using neat vegetable oil showed promising results, longer tests led to injector coking, more engine deposits, ring sticking, and thickening of the engine lubricant. These experiences led to the use of modified vegetable oil as a fuel.

Technical aspects of biodiesel are close to petroleum diesel, such as physical and chemical characteristics of methyl esters related to its performance in compression ignition engines (Saucedo, 2001). Compared with transesterification, pyrolysis has more advantages. The liquid fuel produced from pyrolysis has similar chemical components to conventional petroleum diesel fuel (Zhenyi *et al.*, 2004).

### 3.4.2.4 Pyrolysis and Catalytic Cracking

Pyrolysis is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst (Sonntag, 1979). It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules (Weisz *et al.*, 1979). The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids, and methyl esters of fatty acids.

Soybean oil was thermally decomposed and distilled in air and nitrogen sparged with a standard ASTM distillation apparatus (Niehaus *et al.*, 1986; Schwab *et al.*, 1988). The main components were alkanes and alkenes, which accounted for *ca.* 60% of the total weight. Carboxylic acids accounted for another 9.6 to 16.1%.

Catalytic cracking of vegetable oils to produce biofuels has been studied (Pioch *et al.*, 1993). Copra oil and palm oil stearin were cracked over a standard petroleum catalyst  $\text{SiO}_2/\text{Al}_2\text{O}_3$  at 723 K to produce gases, liquids, and solids with

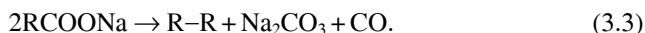
lower molecular weights. The condensed organic phase was fractionated to produce biogasoline and biodiesel fuels.

### 3.5 New Engine Fuels from Vegetable Oils

Vegetable oils as alternative fuels can be used for diesel engines. Due to the rapid decline in crude oil reserves, the use of vegetable oils as diesel fuels is again being promoted in many countries. The effect of coconut oil as a diesel fuel alternative or as direct fuel blends is being investigated using a single-cylinder, direct-injection diesel engine (Machacon *et al.*, 2001).

Vegetable oils have the potential to substitute a fraction of petroleum distillates and petroleum-based petrochemicals in the near future. Vegetable oil fuels are not petroleum-competitive fuels because they are more expensive than petroleum fuels. However, with recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in using vegetable oils in diesel engines.

The soaps obtained from vegetable oils can be pyrolyzed into hydrocarbon-rich products (Demirbas, 2002b). Pyrolysis of Na-soaps may be carried out on vegetable oil products as follows:



The soaps obtained from the vegetable oils can be pyrolyzed into hydrocarbon-rich products according to Eq. (3.3) with higher yields at lower temperatures (Demirbas, 2002b). Table 3.9 shows the yields of pyrolysis products from used sunflower oil sodium soaps at different temperatures. These findings are in general agreement with results given in the literature (Barsic and Humke, 1981).

**Table 3.9** Yields of pyrolysis products from sunflower oil sodium soaps at different temperatures (% by weight)

400 K	450 K	500 K	520 K	550 K	570 K	590 K	610 K
2.8	8.4	29.0	45.4	62.4	84.6	92.7	97.5

#### 3.5.1 Pyrolysis of Vegetable Oils and Fats

Pyrolysis/cracking, defined as the cleavage to smaller molecules by thermal energy, of vegetable oils over petroleum catalysts has been investigated (Madras *et al.*, 2004). Because of the possibility of producing triglycerides in a wide variety of products by high-temperature pyrolysis reactions, many investigators have studied the pyrolysis of triglycerides to obtain products (liquid, gas, and solid)

suitable for fuel under different reaction conditions with and without catalyst (Dykstra *et al.*, 1988; Agra *et al.*, 1992; Adjaye *et al.*, 1995, 1996; Dandik and Aksoy, 1998; Bhatia *et al.*, 1999; Lima *et al.*, 2003; Bhatia *et al.*, 2003).

Pyrolysis is difficult to precisely define, especially when applied to biomass. The older literature generally equates pyrolysis with carbonization, in which the principal product is a solid char by very slow pyrolysis. Currently, the term pyrolysis often describes processes in which oils are preferred products. The time frame for pyrolysis is much faster for the latter process (Mohan *et al.*, 2006).

Pyrolysis is the thermal degradation of vegetable oils by heat in the absence of oxygen, which results in the production of alkanes, alkenes, alkadienes, carboxylic acids, aromatics, and small amounts of gaseous products. Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis, and flash pyrolysis.

Pyrolysis of triglycerides has been investigated for more than 100 years, especially in areas of the world that lack deposits of petroleum (Zhenyi *et al.*, 2004). Pyrolysis of used sunflower oil was carried out in a reactor equipped with a fractionating packed column at 673 and 693 K in the presence of sodium carbonate (1, 5, 10, and 20% based on oil weight) as a catalyst. The conversion of oil was high (42 to 83 wt.%) and the product distribution depended strongly on the reaction temperature, residence times, and catalyst content. The pyrolysis products consisted of gas and liquid hydrocarbons, carboxylic acids, CO, CO<sub>2</sub>, H<sub>2</sub>, and water (Dandik and Aksoy, 1996).

There are several parameters that should be controlled during experiments such as temperature, residence times, and catalyst content. The three vegetable oils (soybean, palm, and castor oils) were pyrolyzed to obtain light fuel products at 503 to 673 K (Lima *et al.*, 2004). These results show that soybean, palm, and castor oils present a similar behavior depending on the pyrolysis temperature range. On the other hand, palm oil reacts in a lower temperature range with a higher yield in the heavy fraction (Lima *et al.*, 2004). A short pyrolysis time (less than 10 s) leads to a high amount of alkanes, alkenes, and aldehydes instead of carboxylic acids. On the other hand, higher temperature and long pyrolysis times do not favor an pyrolysis of this material. In this case, a process like desorption becomes more likely than the pyrolytic process. The liquid products can be improved by deoxygenation in order to obtain an enriched hydrocarbon diesel-like fuel (Lima *et al.*, 2004; Fortes and Baugh, 1999). The parameters of the pyrolysis systematically affect the pyrolytic process.

Increasing Na<sub>2</sub>CO<sub>3</sub> content and temperature increases the formation of liquid hydrocarbon and gas products and decreases the formation of aqueous-phase, acid-phase, and coke-residual oil. The highest C<sub>5</sub>–C<sub>11</sub> yield (36.4%) was obtained using 10% Na<sub>2</sub>CO<sub>3</sub> and a packed column of 180 mm at 693 K. The use of a packed column increased the residence times of the primer pyrolysis products in the reactor and packed column by the fractionating of the products, which caused the additional catalytic and thermal reactions in the reaction system and increased the content of liquid hydrocarbons in the gasoline boiling range (Dandik and Aksoy, 1996).

The HHV of pyrolysis oil from vegetable oils is pretty high. The HHV of pyrolysis oil from rapeseed (38.4 MJ/kg) is slightly lower than that of gasoline (47 MJ/kg), diesel fuel (43 MJ/kg), or petroleum (42 MJ/kg) but higher than coal (32–37 MJ/kg) (Sensoz and Angin, 2000).

### 3.5.1.1 Catalytic Pyrolysis of Sunflower Oil

Table 3.10 shows the yields of  $\text{ZnCl}_2$  catalytic pyrolysis from sunflower oil at different temperatures (Demirbas, 2003c). The yield of conversion into products of  $\text{ZnCl}_2$  catalytic pyrolysis from sunflower oil increased with increases in reaction temperature. The yield of conversion into products from sunflower oil reached a maximum of 78.3% at 660 K. The decrease in yield of conversion could probably be due to higher coke and gas formation at pyrolysis temperatures higher than 660 K. As more coke deposited on the catalyst's surface, the effect of pyrolysis diminished. The gasoline content reached a maximum (35.8% of the conversion products) at 660 K. The aromatic and gas oil contents of conversion products showed a similar trend (Demirbas, 2003c).

**Table 3.10** Yields of  $\text{ZnCl}_2$  catalytic pyrolysis from sunflower oil (SFO) at different temperatures

Temperature (K)	610	630	650	660	670	690
Conversion, wt.% of SFO	35.6	60.7	71.5	78.3	74.9	68.4
Gaseous product, wt.%	3.4	5.1	6.4	7.0	8.9	10.6
Aromatic content, wt.%	8.5	9.3	9.0	9.6	8.2	8.8
Gasoline content, wt.%	28.6	30.4	29.4	35.8	32.7	29.3
Gas oil content, wt.%	6.6	7.3	8.4	10.7	8.6	7.9
Coke residue, wt.%	0.2	0.3	0.4	0.5	2.4	6.8
Water formation, wt.%	3.4	3.7	4.1	4.5	4.1	3.8
Unidentified, wt.%	49.3	43.9	42.3	31.9	35.1	32.8

### 3.5.2 Cracking of Vegetable Oils

The thermal degradation of aliphatic long-chain compounds is known as cracking. Higher-molecular-weight molecules generally convert into smaller-molecular-weight molecules by the cracking process. Large alkane molecules are converted into smaller alkanes and some hydrogen in the cracking process. Smaller hydrocarbons can be obtained by a hydrocracking process. The hydrocracking is carried out in the presence of a catalyst and hydrogen, at high pressure and at much lower temperatures (525 to 725 K).

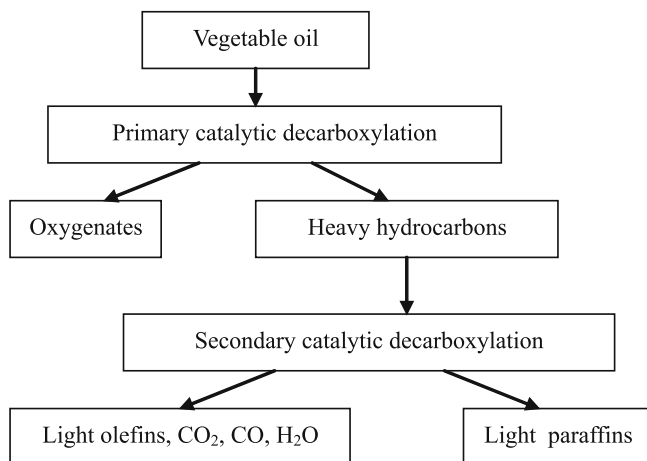
Higher boiling petroleum fractions (typically gas oil) are obtained from silica-alumina catalytic cracking at 725 to 825 K and under lower pressure. The catalytic cracking not only increases the yield of gasoline by breaking large molecules into smaller ones but also improves the quality of the gasoline: this process involves carbocations (the carbocation, a group of atoms that contains a carbon atom bearing only six electrons).

Palm oil stearin and copra oil was subjected to conversion over different catalysts like silica-alumina and zeolite Pioch *et al.*, 1993). It was found that the conversion of palm and copra oil was 84 wt.% and 74 wt.%, respectively. The silica-alumina catalyst was highly selective for obtaining aliphatic hydrocarbons, mainly in the kerosene boiling point range (Katikaneni *et al.*, 1995). The organic liquid products obtained with a silica-alumina catalyst contained between 4 and 31 wt.% aliphatic hydrocarbons and 14 and 58 wt.% aromatic hydrocarbons. The conversion was high and ranged between 81 and 99 wt.%. Silica-alumina catalysts are suitable for converting vegetable oils into aliphatic hydrocarbons. Zinc chloride catalyst, as a Lewis acid, contributed to hydrogen transfer reactions and the formation of hydrocarbons in the liquid phase. Palm oil was converted into hydrocarbons using a shape selective zeolite catalyst (Leng *et al.*, 1999). Palm oil can be converted into gasoline, diesel and kerosene, light gases, coke and water with a yield of 70 wt.%. The maximum yield of gasoline-range hydrocarbons was 40 wt.% of the total product.

Palm oil has been cracked at atmospheric pressure at a reaction temperature of 723 K to produce biofuel in a fixed-bed microreactor. The reaction was carried out over microporous HZSM-5 zeolite, mesoporous MCM-41, and composite micromesoporous zeolite as catalysts. The products obtained were gas, organic liquid, water, and coke. The organic liquid product was composed of hydrocarbons corresponding to the gasoline, kerosene, and diesel boiling point ranges. The maximum conversion of palm oil, 99 wt.%, and gasoline yield of 48 wt.% was obtained with composite micromesoporous zeolite (Sang *et al.*, 2003). Table 3.9 presents the conversion of palm oil over HZSM-5 with different Si/Al ratios of catalyst by catalytic cracking. The gasoline yield increased with an increase in the Si/Al ratio due to the decrease in the secondary cracking reactions and the drop in the yield of gaseous products (Sang *et al.*, 2003). The vegetable oils could be converted into liquid products containing gasoline-boiling-range hydrocarbons. The results show that the product compositions are affected by catalyst content and temperature.

### 3.5.3 Pyrolysis Mechanisms of Vegetable Oils

Pyrolysis involves thermal degradation of biomass by heat in the absence of oxygen, which results in the production of charcoal (solid), bio-oil (liquid), and fuel gaseous products. The pyrolysis of biomass has been studied with the ultimate objective of recovering a biofuel with a medium-low heating value (Maschio *et al.*, 1992; Barth, 1999; Bridgwater *et al.*, 1999).



**Fig. 3.3** Reaction pathway of catalytic decarboxylation of vegetable oils

Soybean, rapeseed, sunflower, and palm oils are the most studied for the preparation of bio-oil. In one study, the viscosity of the distillate was  $10.2 \text{ mm}^2/\text{s}$  at 311 K, which is higher than the ASTM specification for D2 fuel ( $1.9$  to  $4.1 \text{ mm}^2/\text{s}$ ) but considerably below that of soybean oil ( $32.6 \text{ mm}^2/\text{s}$ ). Cottonseed oil used in the cooking process was decomposed with  $\text{Na}_2\text{CO}_3$  as catalyst at 725 K to give a pyrolyzate containing mainly C8–20 alkanes (69.6%) in addition to alkenes and aromatics. The pyrolyzate had a lower viscosity, pour point, and flash point than D2 fuel and equivalent heating values (Bala, 2005).

A mechanism for catalytic decarboxylation of vegetable oils is presented in Fig. 3.3. Vegetable oils contain mainly palmitic, stearic, oleic, and linoleic acids. These fatty acids underwent various reactions, resulting in the formation of different types of hydrocarbons.

The variety of reaction paths and intermediates makes it difficult to describe the reaction mechanism. In addition, the multiplicity of possible reactions of mixed triglycerides makes pyrolysis reactions more complicated (Zhenyi *et al.*, 2004). Generally, thermal decomposition of triglycerides proceeds through either a free-radical or carbonium ion mechanism (Srivastava and Prasad, 2000). Vegetable oil is converted into lower molecular products by two simultaneous reactions: cracking and condensation. The heavy hydrocarbons produced from primary and secondary deoxygenation and cracking yield light olefins and light paraffins, water, carbon dioxide, and carbon monoxide. Hydrocarbon formation can be identified as deoxygenation, cracking, and aromatization with H-transfer. Deoxygenation can take place via decarboxylation and dehydration (Chang and Silvestri, 1977).

The distribution of pyrolysis products depends on the dynamics and kinetic control of different reactions. The maximum gasoline fraction can be obtained under appropriate reaction conditions. Thermodynamic calculation shows that the

initial decomposition of vegetable oils occurs with the breaking of C–O bonds at lower temperatures, and fatty acids are the main product. The pyrolysis temperature should be higher than 675 K; at this temperature, the maximum diesel yield with high oxygen content can be obtained (Zhenyi, 2004). The effect of temperature, the use of catalysts, and the characterization of the products have been investigated (Srivastava and Prasad, 2000). In pyrolysis, the high-molecular-weight materials are heated to high temperatures, so their macromolecular structures are broken down into smaller molecules and a wide range of hydrocarbons are formed. These pyrolytic products can be divided into a gas fraction, a liquid fraction consisting of paraffins, olefins and naphthenes, and solid residue (Demirbas, 2004a). The cracking process yields a highly unstable low-grade fuel oil that can be acid-corrosive, tarry, and discolored along with a characteristically foul odor (Demirbas, 2004b).

It was proposed that thermal and catalytic cracking of triglyceride molecules occurs at the external surface of the catalysts to produce small molecular size components, comprised mainly of heavy liquid hydrocarbons and oxygenates (Leng *et al.*, 1999). In general, it is assumed that the reactions occur predominantly within the internal pore structure of a zeolite catalyst.

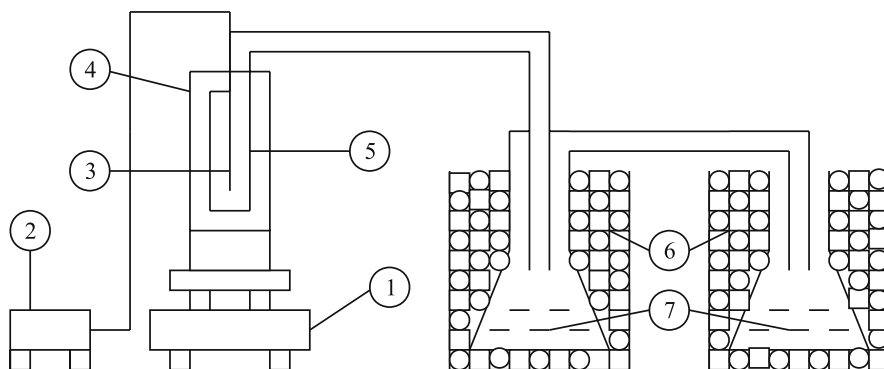
The catalyst acidity and pore size affect the formation of aromatic and aliphatic hydrocarbons. Hydrogen transfer reactions, essential for hydrocarbon formation, are known to increase with catalyst acidity. The high acid density of  $\text{ZnCl}_2$  catalysts contribute greatly to high amounts of hydrocarbons in the liquid product.

### 3.6 Gasoline-rich Liquid from Sunflower Oil by Alumina Catalytic Pyrolysis

Recycling and rerefining are the applicable processes for upgrading of vegetable oils by converting them into reusable products such as gasoline and diesel fuel. Possible acceptable processes are transesterification, cracking, and pyrolysis (Nagai and Seko, 2000; He *et al.*, 2007). Samples of sunflower seed oil were used in the experiments. The sunflower oils were obtained from commercial sources and used without further purification. Aluminum oxide ( $\text{Al}_2\text{O}_3$ , also known as alumina) was obtained from bauxite by a caustic leach method. The catalyst was treated with 10% sodium hydroxide solution before being used in the pyrolysis. 2.5 g of NaOH and 25 g alumina ( $\text{Al}_2\text{O}_3$ ) were added to 250 ml of deionized water and stirred into a water bath for 45 min. 0.5 g of  $\text{AlCl}_3$  was slowly added to the mixture and stirred vigorously for 30 min. The solid material was thoroughly washed, filtered, dried at room temperature overnight, and then calcined at 850 K for 6 h.

The pyrolysis experiments were performed in a laboratory-scale apparatus. The main element of this device was a vertical cylindrical reactor of stainless steel (127.0 mm height, 17.0 mm inner diameter, and 25.0 mm outer diameter) inserted vertically into an electrically heated furnace and provided with an electrical





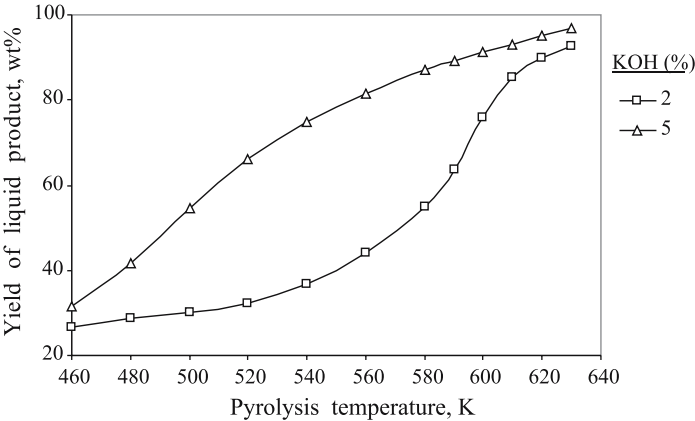
**Fig. 3.4** Simplified device of catalytic pyrolysis. (1) Digital balance, (2) Temperature transmitter, (3) Thermocouple, (4) External heater, (5) Steel reaction vessel, (6) Ice bath, and (7) Collection vessels for liquid products

heating system power source. Figure 3.4 shows the simplified device of the catalytic pyrolysis. The average heating rate was 5 K/min.

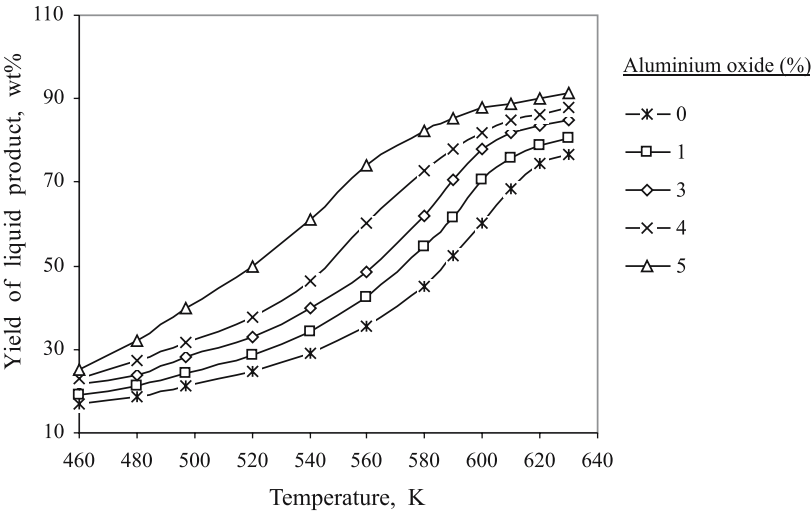
Heat to the vertical cylindrical reactor was supplied from an external heater and the power was adjusted to give an appropriate heat-up time. A simple thermocouple (NiCr – Constantan) or a 360° thermometer with mercury was placed directly in the pyrolysis medium. For each run, the heater was started at 298 K and terminated when the desired temperature was reached. The sunflower seed oil samples were treated with 3% sodium hydroxide solutions in a separatory funnel and then washed with water before pyrolysis. The catalyst (1, 3, 4, and 5% by weight of the used sample) was used in the pyrolysis experiments. In addition, the sunflower seed oil samples were pyrolyzed in catalytic runs with 2 and 5% potassium hydroxide. The pyrolysis products were collected within three different groups as condensable liquid products, non-condensable gaseous products, and solid residue. The liquid product was collected in two glass traps with a cooled ice–salt mixture and ice, respectively. The gas products were trapped over a saturated solution of NaCl in a gas holder.

Figure 3.5 shows the plots for yield of liquid products from pyrolysis of the sunflower oil at different temperatures in the presence of KOH. The nominal pyrolysis time was 30 min. The yields of liquid products increase with increasing temperature and amounts of KOH. The yield sharply increases between 580 and 610 K and then reaches a plateau value with a 2% KOH run. Qualitative observations show that the pyrolytic liquid products from the runs with KOH are highly viscous by comparing the waste-cooking sunflower oil. The repolymerization degree of the pyrolytic liquid products increases with increasing temperature.

Figure 3.6 shows the plots for the yields of liquid products from pyrolysis of sunflower oil at different temperatures in the presence of aluminum oxide catalyst. The catalyst was treated with 10% sodium hydroxide solution before use in the pyrolysis. Particle size of the catalyst was 80 to 120 mesh. The yields of liquid products generally increase with increasing temperature and the percent of catalyst.



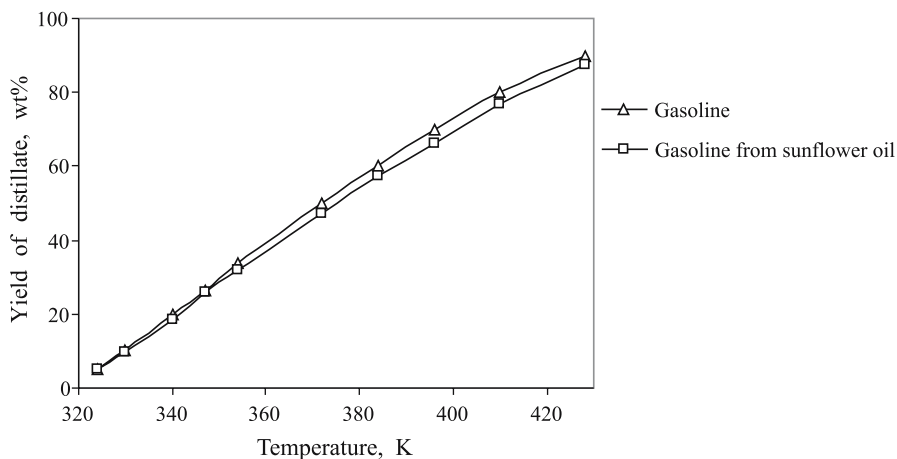
**Fig. 3.5** Yield of liquid products from pyrolysis of sunflower oil at different temperatures in presence of KOH. Pyrolysis time: 30 min



**Fig. 3.6** Yield of liquid products from pyrolysis of sunflower oil at different temperatures in the presence of aluminum oxide. Pyrolysis time: 30 min. Particle size: 80–120 mesh

Figure 3.6 shows how the yield of liquid product from sunflower oil sharply increases between 500 and 680 K in 5% catalytic runs. The yields from non-catalytic runs were 22.1 and 76.8% at 500 and 630 K, respectively. The yields from 5% catalytic runs were 39.8 and 91.4% at 500 and 630 K, respectively. The yields of liquid products reach plateau values between 600 and 630 K.

The liquid products from pyrolysis of used samples have gasolinelike fractions. Table 3.11 shows the average gasoline percentages of liquid products from pyrolysis of sunflower seed oil at different temperatures in the presence of



**Fig. 3.7** Distillation of gasoline and sunflower oil gasoline

**Table 3.11** Average gasoline percentages of liquid products from pyrolysis of sunflower seed oil at different temperatures in the presence of aluminum oxide

Al <sub>2</sub> O <sub>3</sub> (%)	560 K	580 K	600 K	620 K	630 K
0	5.7	9.6	11.8	13.7	16.8
1	12.5	19.3	23.7	27.9	32.5
3	17.3	23.5	28.4	32.8	38.2
4	24.9	29.4	33.9	38.7	47.4
5	33.5	39.6	42.5	48.1	53.8

sodium-hydroxide-treated aluminum oxide. As seen from Table 3.11, the properties of liquid products obtained from catalytic pyrolysis are similar to those of gasoline. The highest yields of gasoline were 53.8% for the gasoline from sunflower oil, which can be obtained from pyrolysis with 5% catalytic runs.

Figure 3.7 shows the curves of distillation of petroleum-based gasoline and gasoline from sunflower oil. The distillation curve of the gasoline from used lubricant oil by catalytic pyrolysis is similar to that of gasoline. Petroleum-based gasoline is slightly more volatile than sunflower oil gasoline.

### 3.7 Diesel-like Fuel from Tallow (Beef) by Pyrolysis and Steam Reforming

Tallow is a mixture of triglycerides, most of which are saturated; tristearin is usually the major component (Ma and Hanna, 1999). The tallow from animal sources is commonly used in soap production. In tallow the saturated fatty acid component accounts for almost 50% of the total fatty acids. The higher palmitic

and stearic acid contents give tallow its unique properties of high melting point and high viscosity.

The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil. Since World War I, many investigators have studied the pyrolysis of vegetable oils to obtain products suitable for fuel. In 1947, large-scale thermal cracking of tung oil calcium soaps was reported (Chang and Wan, 1947).

Used cottonseed oil from the cooking process was decomposed with  $\text{Na}_2\text{CO}_3$  as catalyst at 725 K to give a pyrolyzate containing mainly  $\text{C}_{8-20}$  alkanes (69.6%) in addition to alkenes and aromatics. The pyrolyzate had lower viscosity, pour point, and flash point than D2 fuel and equivalent heating values (Bala, 2005).

Vegetable oil is converted into lower-molecular-weight products by two simultaneous reactions: cracking and condensation. The heavy hydrocarbons produced from primary and secondary deoxygenation and cracking are used to produce light olefins and light paraffins, water, carbon dioxide, and carbon monoxide. Hydrocarbon formation can be identified as deoxygenation, cracking, and aromatization with hydrogen transfer. Deoxygenation can take place via decarboxylation and dehydration (Change and Silvestri, 1977).

Certain petroleum fractions are converted into other kinds of chemical compounds. Catalytic isomerization converts straight-chain alkanes into branched-chain ones. The cracking process converts higher alkanes and alkenes, and thus increases the gasoline yield. The process of catalytic reforming converts alkanes and cycloalkanes into aromatic hydrocarbons and thus increases the gasoline yield. The process of catalytic reforming converts alkanes and cycloalkanes into aromatic hydrocarbons and thus provides the chief raw material for the large-scale synthesis of another broad class of compounds (Ramachandra, 2004).

Crude tallow (beef) samples were used in pyrolysis and steam-reforming procedures. The pyrolysis experiments were performed in a device designed for this purpose. The main element of this device was a tubular reactor of height 95.1 mm, ID 17.0 mm, and OD 19.0 mm inserted vertically into an electrically heated tubular furnace. Pyrolysis was carried out at heating rates of 10 K/s. For each run, the heater was started at ambient temperature and switched off when the desired temperature was reached. Pyrolysis runs were carried out on samples up to 5 g in a temperature range of 775 to 1025 K. The yields of pyrolysis products were determined gravimetrically by weighing the different fraction of char and oily products and of the gaseous fraction by a gas meter. The accuracy in the determination of the yields was about 3%. The temperature of the reaction vessel was measured with an iron-constantan thermocouple and controlled at  $\pm 3$  K. The experiments were performed at 775, 775, 825, 875, 925, 975, and 1025 K. The steam reforming was performed in a 100-mL cylindrical autoclave made of 316 stainless steel. The sample was loaded from the bolt hole into the autoclave, and the hole was plugged with a screw bolt after each run. The experiments were carried out at 650, 700, 750, 800, and 850 K at various ratios of water to tallow: 0.5, 1.0, 1.5, and 2. At the end of every experiment, the heat was turned off and, once room temperature was reached, the carbonaceous residue (char) remaining and the condensed liquid in the collected apparatus of liquids could be weighed. The autoclave was

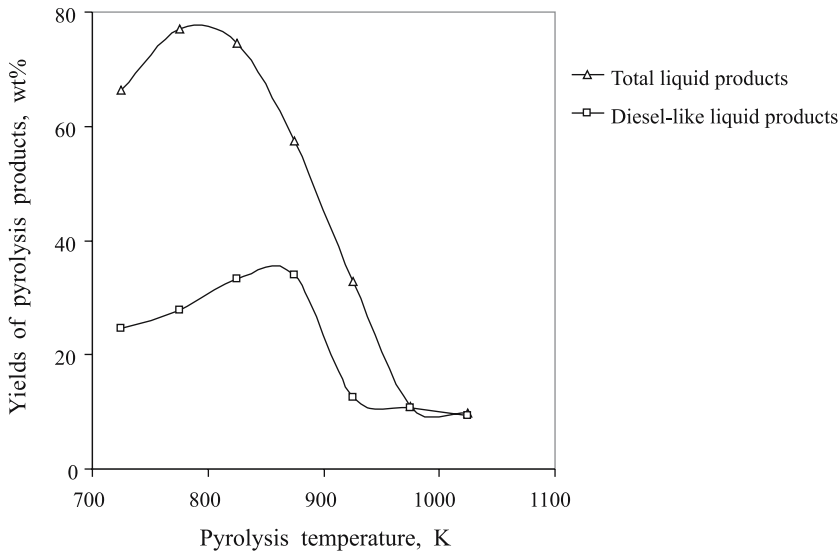
supplied with heat from an external heater, and power was adjusted to give an approximate heating time of 60 min. The temperature of the reaction vessel was measured with an iron-constantan thermocouple and controlled at  $\pm 5$  K. Reactions occurred during the heating period. After each run, the gas was vented and the autoclave was poured into a beaker. The rest of the oil and solids were removed from the autoclave by washing with used solvent. The products were recovered by washing with hot water. The obtained mixture was then filtered in a 30-mL glass crucible, with a medium frit, to separate the solvent and insoluble materials. The preweighed filter was dried to constant weight in an oven at 378 K.

Table 3.12 shows the average composition of fatty acids in tallow. The total fatty acids in the tallow samples were 51.1% by weight. The major fatty acids in the tallow were palmitic (28.7%), stearic (19.5), and oleic (44.4%). Higher palmitic and stearic acid contents give the tallow a high melting point.

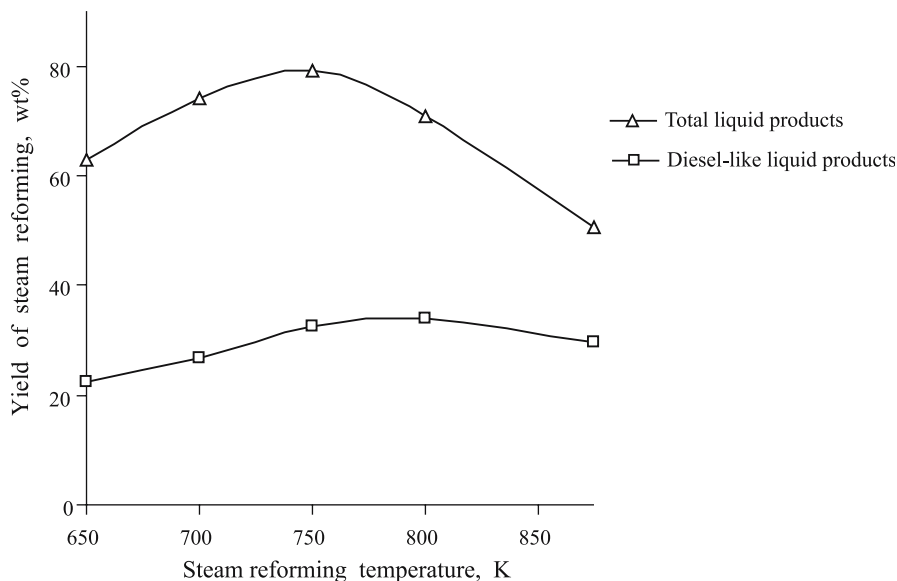
Figure 3.8 shows the effect of temperature on total liquid and diesel-like liquid yields from tallow by pyrolysis. The reaction parameters of pyrolysis are tempera-

**Table 3.12** Average composition of fatty acids in tallow (wt.%)

Fatty acid	%
Myristic (14:0)	2.9
Palmitic (16:0)	28.7
Stearic (18:0)	19.5
Oleic (18:1)	44.4
Linoleic (18:2)	3.6
Linolenic (18:3)	0.9



**Fig. 3.8** Effect of temperature on total liquid and diesel-like liquid yields from tallow by pyrolysis (reaction time: 45 min)



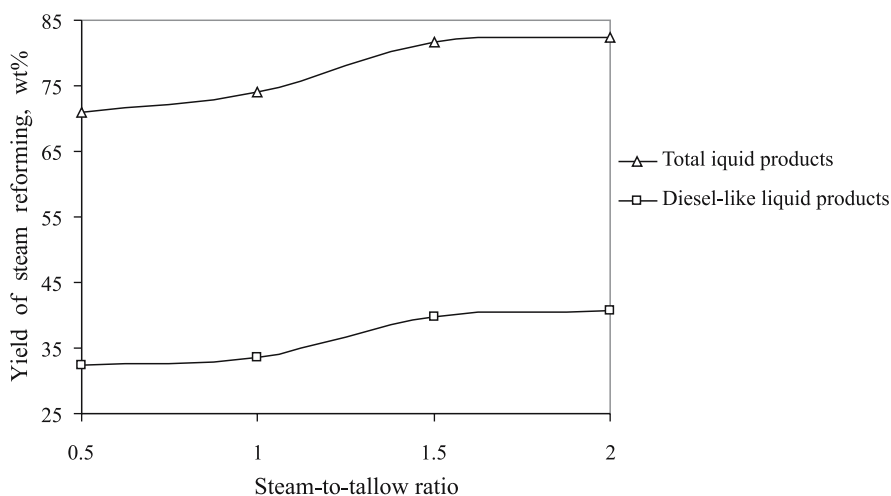
**Fig. 3.9** Effect of temperature on total liquid and diesel-like liquid yields from tallow by steam reforming (reaction time: 45 min; steam-to-tallow ratio: 0.5)

ture and resistance time. The maximum total liquid product obtained from pyrolysis was 77.1% at 775 K. The yield of diesel-like liquid from pyrolysis of the tallow increases from 24.6 to 33.9% with increasing temperature from 725 to 875 K and then sharply decreases.

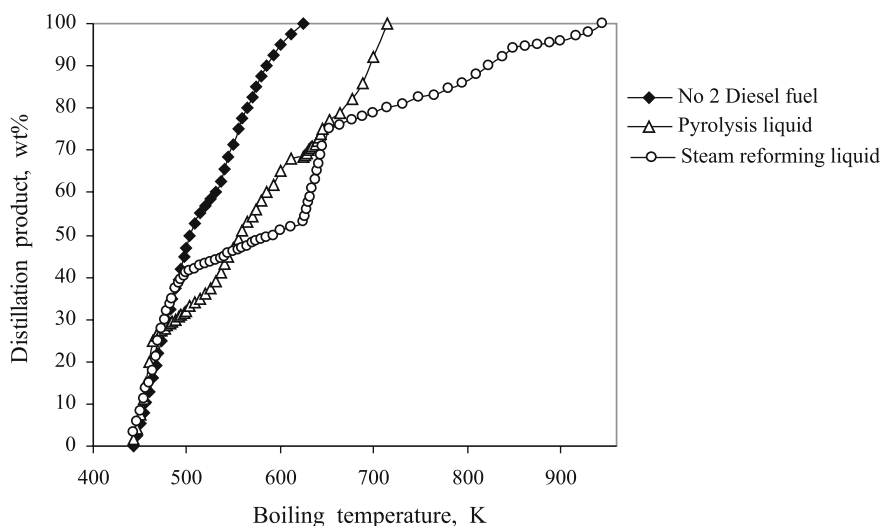
Figure 3.9 shows the effect of temperature on total liquid and diesel-like liquid yields from tallow by steam reforming. The reaction parameters of steam reforming are temperature, ratio of steam to tallow and resistance time. The maximum total liquid product obtained from steam reforming was 79.1% at 750 K. The yield of diesel-like liquid from steam reforming of the tallow increases from 22.3 to 34.1% when temperature is increased from 650 to 800 K and then slightly decreases.

Figure 3.10 shows the effect of the steam-to-tallow ratio on total liquid and diesel-like liquid yields from tallow by steam reforming. The yields of diesel-like liquid from steam reforming increase from 32.4 to 40.6% when the (water/tallow) ratio increases from, respectively, 0.5 to 2 at a liquefaction temperature of 800 K.

Figure 3.11 shows the comparison of distillation curves of average distillation products obtained from pyrolysis and steam reforming of tallow to that of D2 fuel. As can be seen from the figure, the first distillation products of 25 and 40% from pyrolysis and steam reforming, respectively, are similar to the distillation product from D2 fuel.



**Fig. 3.10** Effect of steam-to-tallow ratio on total liquid and diesel-like liquid yields from tallow by supercritical water liquefaction (reaction time: 45 min; temperature: 800 K)



**Fig. 3.11** Comparison of distillation curves of average distillation products obtained from pyrolysis and steam reforming of tallow to that of D2 fuel

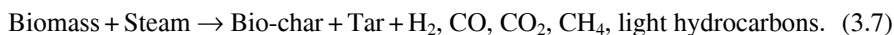
### 3.8 Converting Triglyceride-derived Synthetic Gas to Fuels via Fischer–Tropsch Synthesis

Gasification is a thermochemical conversion of a biomass fuel to a gaseous fuel with a gasification agent such as air, oxygen, steam, carbon dioxide, or mixtures

of these to produce a combustible gas such as hydrogen, carbon monoxide, or methane. This reaction can be carried out in a fixed bed, a fluidized bed, or entrained flow reactors. The main gasification reactions are:



As reported extensively in the literature, biomass steam gasification results in the conversion of carbonaceous materials into permanent gases ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , light hydrocarbons), char, and tar (Dry, 1981; Rapagna *et al.*, 1998; Stelmachowski and Nowicki, 2003).

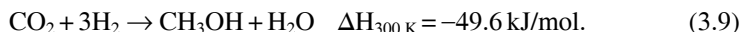
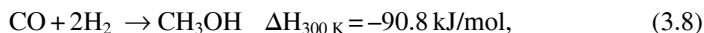


Synthesis gas includes mainly hydrogen and carbon monoxide and is also called syngas ( $\text{H}_2 + \text{CO}$ ). Syngas is a raw material for large scale synthesis for the production of important base products of organic chemistry. The fundamental reactions of synthesis gas chemistry are methanol synthesis, Fischer–Tropsch synthesis (FTS), oxosynthesis (hydroformylation), and methane synthesis (Prins *et al.*, 2004).

To produce syngas from a biomass fuel the following procedures are necessary: (a) gasification of the fuel, (b) cleaning the product gas, (c) using the synthesis gas to produce chemicals, (d) using the synthesis gas as energy carrier in fuel cells.

FTS converts syngas, which can be made from coal, natural gas, biomass, and any carbonaceous materials, into long-chain hydrocarbons. This is an alternative route to obtain fuel and chemicals rather than the current dominant petroleum resources. FTS is now becoming competitive with petroleum due to its improved catalysts and processes.

Methanol, one of the most industrially important chemicals, may be directly used as a clean fuel or as an additive to gasoline. It may be converted into gasoline using a shape-selective (ZSM-5) catalyst. Methanol can be produced from hydrogen-carbon oxide mixtures by means of the catalytic reaction of carbon monoxide and some carbon dioxide with hydrogen:



The presence of a certain amount of  $\text{CO}_2$  in the percentage range, 35 to 55 by volume, is necessary to optimize the reaction. Side reactions, also strongly exothermic, can lead to the formation of byproducts such as methane, dimethylether, or higher alcohols.

Methanol is currently produced on an industrial scale exclusively by catalytic conversion of synthetic gas ( $\text{H}_2 + \text{CO} + \text{CO}_2$ ). Processes are classified according to the operating pressure: (a) low-pressure process (5 to 10 MPa), (b) medium-pressure process (10 to 25 MPa) and (c) high-pressure process (25 to 30 MPa). To produce one ton of methanol,  $2.52 \times 10^3 \text{ m}^3$  of synthesis gas (70%  $\text{H}_2$ , 21%  $\text{CO}$ ,

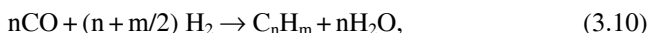


7% CO<sub>2</sub>) is necessary. CO hydrogenation or FTS on cobalt-based catalysts has been studied for over 70 years. Copper and zinc are the key components of methanol synthesis catalysts (Stelmachowski and Nowicki, 2003). Copper-zinc catalysts used in the low-pressure process require a sulfur-free gas ( $H_2S < 1 \text{ mL/m}^3$ ). The catalysts can be deactivated by sulfide ion (catalyst poison). Catalysts (ZnO and Cr<sub>2</sub>O<sub>3</sub> activated with chromic acid) for the medium- and high-pressure processes can accept  $30 \text{ mL/m}^3$  of H<sub>2</sub>S.

Production of methanol with ZnO and Cr<sub>2</sub>O<sub>3</sub> catalysts by the high-pressure process is no longer economical. Instead of these, copper-containing catalysts with higher activity and better selectivity is now used. Sulfur- and chlorine-containing pollution can be prevented by long use of copper-containing catalysts in industrial methanol production. These catalyst poisons must be removed from the feed gas mixture prior to methanol synthesis. The main advantages of the low-pressure process are lower investment and production costs, improved operational reliability, and greater flexibility in the choice of plant size.

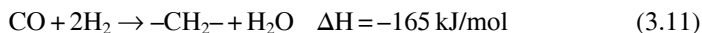
The higher alcohol synthesizes from CO/H<sub>2</sub> mixtures for use as additives to gasoline to increase the octane number. Methanol and higher alcohols can be simultaneously produced from synthesis gas by using many different catalysts such as Cu/Zn, Zr/Fe, and Mo/Th. Similar experimental procedures can be used in FTS, HAS, and methanol synthesis. Three types of reaction are considered for HAS: formation of n-alcohols, formation of n-paraffins, and the water-gas shift.

Biomass can be converted into bio-syngas by non-catalytic, catalytic, and steam-gasification processes. FTS was established in 1923 by German scientists Franz Fischer and Hans Tropsch. The main aim of FTS is the synthesis of long-chain hydrocarbons from a CO and H<sub>2</sub> gas mixture. The FTS is described by the following set of equations (Anderson, 1984; Schulz, 1999; Sie and Krishna, 1999):



where  $n$  is the average length of the hydrocarbon chain and  $m$  is the number of hydrogen atoms per carbon. All reactions are exothermic and the product is a mixture of different hydrocarbons in that paraffin and olefins are the main parts.

In FTS one mole of CO reacts with two moles of H<sub>2</sub> in the presence cobalt (Co)-based catalyst to afford a hydrocarbon chain extension ( $-\text{CH}_2-$ ). The reaction of synthesis is exothermic ( $\Delta H = -165 \text{ kJ/mol}$ ):



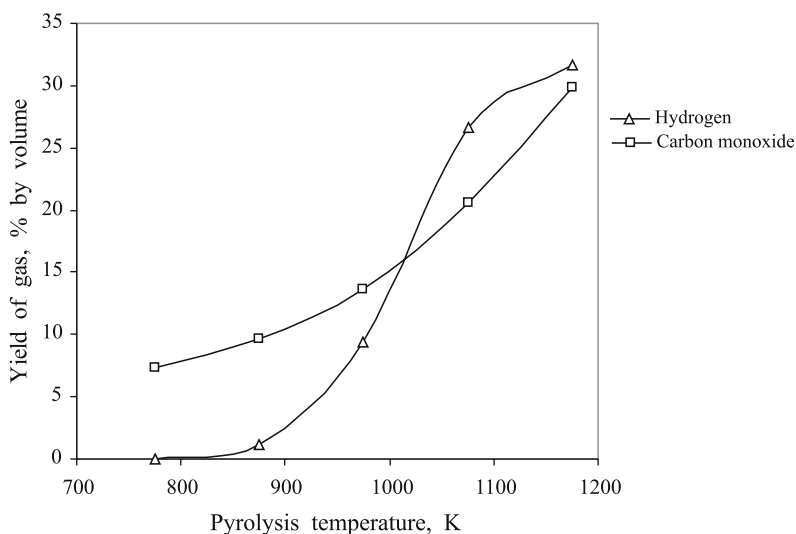
The  $-\text{CH}_2-$  is a building block for longer hydrocarbons. A main characteristic regarding the performance of FTS is the liquid selectivity of the process (Tijmensen *et al.*, 2002). For this reaction, given by Eq. (3.11), a H<sub>2</sub>/CO ratio of at least 2 for the synthesis of the hydrocarbons is necessary. The reaction of the synthesis is exothermic ( $\Delta H = -42 \text{ kJ/mol}$ ).

Typical operation conditions for the FTS are a temperature range of 475 to 625 K and pressures of 15 to 40 bar, depending on the process. All reactions are exothermic. The kind and quantity of liquid product obtained is determined by the reaction temperature, pressure and residence time, type of reactor, and catalyst

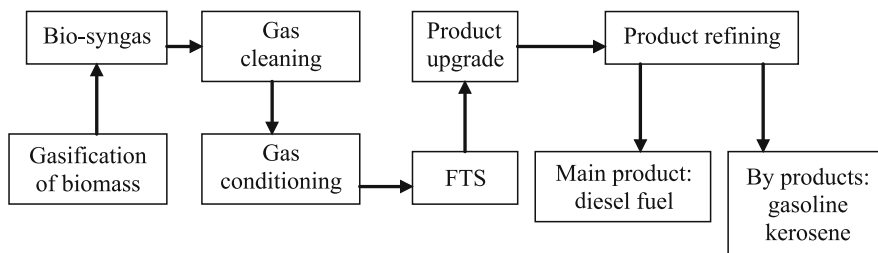
used. Iron catalysts have a higher tolerance for sulfur, are cheaper, and produce more olefin products and alcohols. However, the lifetime of the iron catalysts is short and in commercial installations generally limited to 8 weeks. Cobalt catalysts have the advantage of a higher conversion rate and a longer life (over 5 years). Cobalt catalysts are in general more reactive for hydrogenation and therefore produce fewer unsaturated hydrocarbons and alcohols compared to iron catalysts.

The products from FTS are mainly aliphatic straight-chain hydrocarbons ( $C_xH_y$ ). In addition to  $C_xH_y$ , branched hydrocarbons, unsaturated hydrocarbons, and primary alcohols are also formed in minor quantities. The product distribution obtained from FTS includes the light hydrocarbons methane ( $CH_4$ ), ethene ( $C_2H_4$ ), and ethane ( $C_2H_6$ ), LPG ( $C_3$ – $C_4$ , propane and butane), gasoline ( $C_5$ – $C_{12}$ ), diesel fuel ( $C_{13}$ – $C_{22}$ ), and light waxes ( $C_{23}$ – $C_{33}$ ) (Table 3.1). Raw bio-syngas contains trace contaminants like  $NH_3$ ,  $H_2S$ ,  $HCl$ , dust, and alkalis in ash. The distribution of the products depends on the catalyst and the process parameters such as temperature, pressure, and residence time.

Figure 3.12 shows the yields of hydrogen and carbon monoxide obtained from the pyrolysis of tallow (beef) at different temperatures. Figure 3.12 shows how the yields of hydrogen and carbon monoxide from pyrolysis of tallow increases with increasing temperature. The yield of hydrogen from pyrolysis of the tallow sharply increases from 9.4 to 31.7% by volume of total gaseous products when the temperature is increased from 975 to 1175 K. The yield of carbon monoxide from pyrolysis increases from 20.6 to 26.7% by volume of total gaseous products when the temperature is increased from 1075 to 1175 K.



**Fig. 3.12** Yields of hydrogen and carbon monoxide (% by volume of total gas products) obtained from pyrolysis of tallow (beef) at different temperatures



**Fig. 3.13** Production of diesel fuel from bio-syngas by Fischer–Tropsch synthesis (FTS)

Hydrogen gas can be produced from the biomass material by direct and catalytic pyrolysis while, in one study, the final pyrolysis temperature was generally increased from 775 to 1025 K (Caglar, 2003). Hydrogen- and carbon-monoxide-rich gas products can be obtained from triglycerides by pyrolysis. The total yield of combustible gases (mainly  $H_2$  and CO) for the triglyceride samples increased when the pyrolysis temperature was increased from 775 to 1175 K. The most important reaction parameters were temperature and resistance time.

Figure 3.13 shows the production of diesel fuel from bio-syngas by FTS. The design of a biomass gasifier integrated with a FTS reactor must be aimed at achieving a high yield of liquid hydrocarbons. For the gasifier, it is important to avoid methane formation as much as possible and convert all carbon in the biomass to mainly carbon monoxide and carbon dioxide (Prins *et al.*, 2004).

Gas cleaning is an important process before FTS. Gas cleaning is even more important for the integration of a biomass gasifier and a catalytic reactor. To avoid poisoning of FTS catalysts, tar, hydrogen sulfide, carbonyl sulfide, ammonia, hydrogen cyanide, alkali, and dust particles must be removed thoroughly (Tijmensen *et al.*, 2002).

## 3.9 Triglyceride Analyses

### 3.9.1 Viscosity

Viscosity is a measure of the internal fluid friction or resistance of oil to flow, which tends to oppose any dynamic change in the fluid motion (Song, 2000). As the temperature of oil increases, its viscosity decreases, and it is therefore able to flow more readily. It is also important for the flow of oil through pipelines, injector nozzles, and orifices (Radovanovic *et al.*, 2000). The lower the viscosity of the oil, the easier it is to pump and atomize and achieve finer droplets (Islam *et al.*, 2004).

Viscosity is measured on several different scales, including Redwood No. 1 at 100 F, Engler Degrees, Saybolt Seconds, *etc.* Viscosity is the most important

property of biofuel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. Biodiesel has a viscosity close to that of diesel fuels. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors.

Vegetable oils are extremely viscous with viscosities 10 to 20 times greater than that of D2 fuel. Castor oil is in a class by itself with a viscosity of more than 100 times that of D2 fuel (Demirbas, 2003). The viscosity of oil can be lowered by blending it with pure ethanol. To reduce the high viscosity of vegetable oils, microemulsions with immiscible liquids such as methanol and ethanol and ionic or non-ionic amphiphiles have been studied (Ramadhas *et al.*, 2004; Mittelbach and Gangl, 2001). Short engine performances of both ionic and non-ionic microemulsions of ethanol in soybean oil were nearly as good as that of D2 fuel. All microemulsions with butanol, hexanol, and octanol met the maximum viscosity requirement for D2 fuel. 2-octanol was found to be an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil.

### 3.9.2 Density

Density is another important property of biofuel. Density is the mass per unit volume of any liquid at a given temperature. Specific gravity is the ratio of the density of a liquid to the density of water. Density has importance in diesel-engine performance since fuel injection operates on a volume metering system (Song, 2000). Also, the density of the liquid product is required for the estimation of the Cetane index (Srivastava and Prasad, 2000). In one study, densities were determined using a density meter at 298 K according to ASTM D5002-94. The density meter was calibrated using reverse osmosis water at room temperature.

### 3.9.3 Cetane Number

The cetane number (CN) is a measure of ignition quality or ignition delay and is related to the time required for a liquid fuel to ignite after injection into a compression ignition engine. CN is based on two compounds, namely, hexadecane, with a cetane of 100, and heptamethylnonane, with a cetane of 15. The CN scale also shows that straight-chain, saturated hydrocarbons have higher CNs than branched-chain or aromatic compounds of similar molecular weight and number of carbon atoms. The CN relates to the ignition delay time of a fuel upon injection into the combustion chamber. It is a measure of ignition quality of diesel fuels; a high CN implies short ignition delay. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN. The CN of biofuel from animal fats is higher than those of vegetable oils. CN is determined from a real

engine test. The cetane index (CI) is a calculated value derived from the density and volatility obtained from boiling characteristics of a fuel. CI usually gives a reasonably close approximation to a real CN (Song, 2000).

### **3.9.4 Cloud and Pour Points**

Two important parameters for low-temperature applications of a fuel are cloud point (CP) and pour point (PP). The CP is the temperature at which a cloud of crystals first appears in a liquid when cooled under conditions as described in ASTM D2500-91. The PP is the temperature at which the amount of wax from solution is sufficient to gel the fuel; thus it is the lowest temperature at which the fuel can flow. The PP is the lowest temperature at which an oil specimen can still be moved. It is determined according to ASTM D97-96. These two properties are used to specify the cold-temperature usability of a fuel. In one study, two cooling baths with different cooling temperatures were used. Triglycerides have higher CP and PP compared to conventional diesel fuel (Prakash, 1998).

### **3.9.5 Distillation Range**

The distillation range of a fuel affects its performance and safety. It is an important criterion for an engine's start and warmup. It is also needed in the estimation of the CI. The distillation range of the liquid product is determined by a test method (ASTM D2887-97) that covers the determination of the boiling range distribution of liquid fuels.

When the ASTM D86 procedure was used to distil vegetable oils, they cleaved to a two-phase distillate. Preliminary data indicate a complex mixture of products including alkanes, alkenes, and carboxylic compounds (Goering *et al.*, 1982). Typically, it is not possible to distil all of the vegetable oil, and some brownish residue remained in the distillation flask. However, soaps obtained from vegetable oils can be distilled into hydrocarbon-rich products with higher yields. The findings from distillation ranges of vegetable oils are given in the literature (Barsic and Humke, 1981).

### **3.9.6 Heat of Combustion**

The heat of combustion measures the energy content in a fuel. This property is also referred to as calorific value or heating value. Although the CN determines combustion performance, it is the heating value, along with thermodynamic criteria, that sets the maximum possible output of power (Song, 2000). The higher

heating values (HHVs) of oil samples are measured in a bomb calorimeter according to the ASTM D2015 standard method.

The ultimate analysis of a vegetable oil provides the weight percentages of carbon, hydrogen, and oxygen. The carbon, hydrogen, and oxygen contents of various common vegetable oils are 74.5 to 78.4, 10.6 to 12.4, and 10.8 to 12.0 wt.%, respectively. The HHV of vegetable oils (Goering *et al.*, 1982) ranges from 37.27 to 40.48 MJ/kg. The HHVs of various vegetable oils vary by <9%.

The saponification value (SV) of an oil decreases as its molecular weight increases. On the other hand, the percentages of carbon and hydrogen in oil increase as the molecular weight decreases. The increase in the iodine value (IV) (*i.e.*, carbon-carbon double bond,  $\text{--C=C--}$ , content) results in a decrease in the heat content of an oil. Therefore, for calculation of the HHVs (MJ/kg) of vegetable oils, Eq. (3.12) was suggested by Demirbas (1998):

$$\text{HHV} = 49.43 - [0.041(\text{SV}) + 0.015(\text{IV})]. \quad (3.12)$$

### 3.9.7 Water Content

The water content of a fuel is required to accurately measure the net volume of actual fuel in sales, taxation, exchanges, and custody transfer (Srivastava and Prasad, 2000). Various methods are used for the determination of water content in oil samples such as evaporation methods, distillation methods, the xylene method, Karl-Fischer titration method, *etc.* Evaporation methods rely on measuring the mass of water in a known mass of sample. The moisture content is determined by measuring the mass of an oil sample before and after the water is removed by evaporation. Distillation methods are based on direct measurement of the amount of water removed from an oil sample by evaporation. The Karl-Fischer titration method is often used for determining the moisture content of oils that have low water content.

### 3.9.8 Discussion of Fuel Properties of Triglycerides

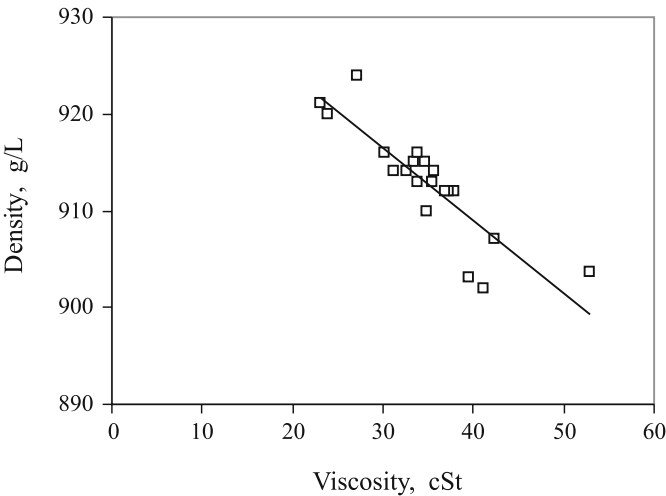
Fuel properties of triglyceride oils were characterized by determining its viscosity, density, cetane number, cloud and pour points, distillation range, flash point, ash content, sulfur content, carbon residue, acid value, copper corrosion, and HHV (Goering *et al.*, 1982). Table 3.13 shows viscosity, density, flash point, and distillation range measurements of 15 vegetable oils. Figure 3.14 shows the relationships between viscosity and density for vegetable oils.

$$D = -0.7503V + 939.04, \quad (3.13)$$

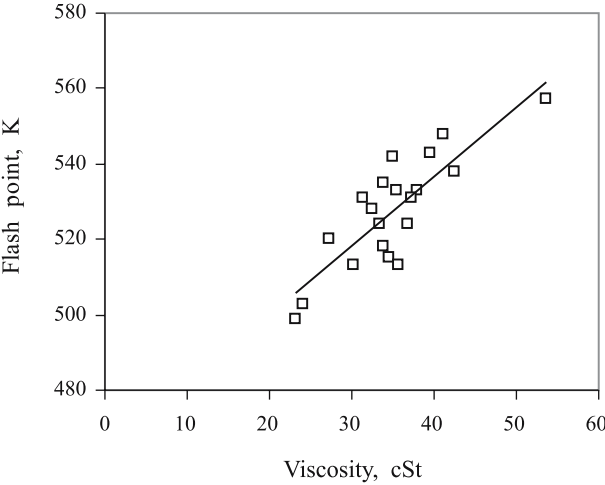
**Table 3.13** Viscosity, density, flash point, and distillation range measurements of 15 vegetable oils

Vegetable oil	Viscosity mm <sup>2</sup> /s	Density g/L	Flash point K	Distillation range K
Ailanthus	30.2	916	513	423–623
Bay laurel	23.2	921	499	418–618
Beech	34.6	915	515	428–633
Beechnut	38.0	912	533	428–636
Corn	34.9	910	542	428–638
Cottonseed	33.5	915	524	443–638
Crambe	53.0	904	557	–
Hazelnut kernel	24.0	920	503	433–623
Linseed	27.2	924	520	438–638
Mustard oil	33.8	913	518	–
Peanut	39.6	903	543	440–644
Poppy seed	42.4	907	538	443–643
Rapeseed	37.3	912	531	–
Safflower seed	31.3	914	531	438–641
H.O. Safflower	41.2	902	548	–
Sesame	35.5	913	533	–
Soybean	32.6	914	528	–
Spruce	35.6	914	513	423–623
Sunflower seed	33.9	916	535	428–634
Walnut kernel	36.8	912	524	433–628

where  $D$  is the density and  $V$  the viscosity of an oil sample (Eq. 3.13). There is considerable regression between viscosity and density values of vegetable oils ( $R^2 = 0.7494$ ).



**Fig. 3.14** Relationship between viscosity and density in vegetable oils



**Fig. 3.15** Relationship between viscosity and flash point in vegetable oils

Figure 3.15 shows the relationship between viscosity and flash point in vegetable oils.

$$F = 1.8512V + 462.66, \tag{3.14}$$

where  $F$  is the flash point and  $V$  the viscosity of an oil sample (Eq. 3.14). There is regression between viscosity and flash point values of vegetable oils ( $R^2 = 0.6996$ ).

The fuel properties of No. 2 petroleum diesel, cottonseed, and linseed oils are given in Table 3.14. It is well known that a double bond in the fatty acid structure increases copper corrosion because it causes inner oxidation or peroxidation during combustion. Therefore double bonds decrease quality. The cottonseed oil was extremely viscous (33 to 36 cSt at 311 K) with viscosities ranging from 12 to 13 times greater than No. 2 petroleum diesel.

**Table 3.14** Fuel properties of No. 2 petroleum diesel, cottonseed, and linseed oils

Property	No. 2 petr. Diesel	Cottonseed oil	Linseed oil
Distillation range (K)	460–620	443–628	438–638
Viscosity (mm <sup>2</sup> /s at 311 K)	2.68–2.72	32–36	26–29
Cetane number	46–48	41–44.0	26–30
Cloud point (K)	257–259	274–276	276–279
Pour point (K)	239–242	257–259	256–259
Carbon residue (% by weight)	0.34–0.48	0.23–0.25	0.23–0.25
Ash content (% by weight)	0.01–0.02	0.008–0.01	0.009–0.01
Sulfur content (% by weight)	0.03–0.06	0.008–0.01	0.008–0.01
Higher heating value (MJ/kg)	45.0–45.3	39.4–39.6	39.6–39.8



The CN scale shows that straight-chain, saturated hydrocarbons have higher CNs compared to branched-chain or aromatic compounds of similar molecular weight and number of carbon atoms. The CN is one of the prime indicators of the quality of diesel fuel. It relates to the ignition delay time of a fuel upon injection into the combustion chamber. The CN is a measure of ignition quality of diesel fuels, and a high CN implies short ignition delay. In one study, the CN of CSO samples were in the range 41 to 44.0 (Table 3.14). The CN of biodiesel is generally higher than conventional diesel. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN. The CN of biodiesel from animal fats is higher than those of vegetable oils (Bala, 2005).

### 3.10 Triglyceride Economy

High petroleum prices spur the study of biofuel production. Lower-cost feedstocks are needed since biodiesel from food-grade oils is not economically competitive with petroleum-based diesel fuel. Inedible plant oils have been found to be promising crude oils for the production of biodiesel.

The cost of biofuel and demand of vegetable oils can be reduced by inedible oils and used oils, instead of edible vegetable oil. Around the world large amounts of inedible oil plants are available in nature.

Vegetable oil is traditionally used as a natural raw material in linoleum, paint, lacquers, cosmetics, and laundry powder additives. There is a growing market in the field of lubricants, hydraulic oils, and special applications. Intensive use of pure plant oil in motors is an option to replace fossil fuels. Nowadays the technique is tested and well established. Pure plant oil fuel has the advantages of low sulfur and aromatic content and safer handling. The use of cold-pressed plant oil instead of fossil diesel leads to a reduction in the production of the greenhouse gas CO<sub>2</sub>.

Everybody can produce their own fuel. The cold-pressing process does not require complicated machinery. The characteristics of this process are low energy requirements without any use of chemical extractive agents.

### References

- Adjaye, J.D., Katikaneni, S.P.R., Bakhsi, N.N. 1995. Catalytic conversion of canola oil to fuels and chemicals over various cracking catalysts. *Can J Chem Eng* 73:484–497.
- Adjaye, J.D., Katikaneni, S.P.R., Bakhsi, N.N. 1996. Catalytic conversion of a biofuel to hydrocarbons: Effect of mixtures of HZSM-5 and silica-alumina catalysts on product distribution. *Fuel Process Technol* 48:115–143.
- Agra, I.B., Warnijati, S., Pratama, M.S. 1992. Catalytic pyrolysis of nyamplung seeds oil to mineral oil like fuel. In: Sayigh, A.A.M. (ed.) *Proceedings of the 2nd World Renewable Energy Congress*. Pergamon, Reading, UK.
- Alencar, J.W., Alves, P.B., Craveiro, A.A. 1983. Pyrolysis of tropical vegetable oils. *J Agric Food Chem* 31:1268–1270.

- Anderson, R.B. 1984. The Fischer-Tropsch synthesis. Academic, New York.
- ASAE., 1982. Vegetable oil fuels. In: Backers, L. (ed.) Proceedings of the international conference on plant and vegetable oils as fuels. ASAE, St. Joseph, MI.
- Association of Official Analytical Chemists (AOAC). 1993. Section C: Commercial Fats and Oils, American Oil Chemists Society (AOCS) official method Cd 1–25 for Iodine Value. Association of Official Analytical Chemists, Washington, D.C.
- Association of Official Analytical Chemists (AOAC). 1997. Section C: Commercial Fats and Oils, American Oil Chemists Society (AOCS) official method Cd 3–25 for Saponification Value. Association of Official Analytical Chemists, Washington, D.C.
- ASTM. 1979. Standard Test Method for Ignition Quality of Diesel Fuels by the Cetane Method, Designation: D 613, Annual Book of ASTM Standards, vol. 05.04, ASTM, Philadelphia, PA.
- ASTM. 1988. Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter, Designation: D2015–85, Annual Book of ASTM Standards, vol. 05.02, ASTM, Philadelphia, PA, pp. 238–243.
- ASTM. 1995a. Standard Test Method for Ash from Petroleum Products, Designation: D482-91, Annual Book of ASTM Standards, vol. 05.01, ASTM, Philadelphia, PA, pp. 198–199.
- ASTM. 1995d. Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence, Designation: D5453-93, Annual Book of ASTM Standards, vol. 05.03, ASTM, Philadelphia, PA, pp. 603–608.
- ASTM D97-96 1998. Standard test method for pour point of petroleum products. In: Annual Book of ASTM Standards, vol. 05.01. ASTM, Philadelphia, PA, pp. 76–79.
- ASTM D5002-94. 1998. Standard test method for calculated cetane index of distillate fuels. In: Annual Book of ASTM Standards, vol. 05.03. ASTM, Philadelphia, PA, pp. 263–266.
- ASTM D2887-97. 1998. Standard test method for boiling range distribution of petroleum fractions by gas chromatography. In: Annual Book of ASTM Standards, vol. 05.03. ASTM, Philadelphia, PA, pp. 195–204.
- Azam, M.M., Waris, A., Nahar, N.M. 2005. Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. *Biomass Bioenergy* 29:293–302.
- Bajpai, S., Prajapati, S., Luthra, R., Sharma, S., Naqvi, A., Kumar, S. 1999. Variation in the seed and oil yields and oil quality in the Indian germplasm of opium poppy *Papaver somniferum*. *Genet Res Crop Evol* 46:435–439.
- Bala, B.K. 2005. Studies on biodiesels from transformation of vegetable oils for diesel engines. *Energy Edu Sci Technol* 15:1–43.
- Barsic, N.J., Humke, A.L. 1981. Performance and emissions characteristics of a naturally aspirated diesel engine with vegetable oil fuels. SAE paper no. 810262. Society of Automotive Engineers, Warrendale, PA.
- Barth, T. 1999. Similarities and differences in hydrous pyrolysis and source rocks. *Org Geochem* 30:1495–1507.
- Bartholomew, D. 1981. Vegetable oil fuel. *JAOCS* 58:286A–288A.
- Becker, E.W. 1994. In: Baddiley, J. *et al.* (eds.) *Microalgae: biotechnology and microbiology*. Cambridge University Press, Cambridge, UK.
- Bhatia S., Twaiq F.A., Zabidi N.A.M. 1999. Catalytic conversion of palm oil to hydrocarbons: Performance of various zeolite catalysts. *Ind Eng Chem Res* 38:3230–3237.
- Bhatia, S., Sang, O.Y., Twaiq, F., Zakaria, R., Mohamed, A.R. 2003. Biofuel production from catalytic cracking of palm oil. *Energy Sour* 25:859–869.
- Bilgin, A., Durgun, O., Sahin Z. 2002. The effects of diesel-ethanol blends on diesel engine performance. *Energy Sour* 24:431–440.
- Billaud, F., Dominguez, V., Broutin, P., Busson C. 1995. Production of hydrocarbons by pyrolysis of methyl esters from rapeseed oil. *J Am Oil Chem Soc* 72:1149.
- Bridgewater, A.V., Meier, D., Radlein, D. 1999. An overview of fast pyrolysis of biomass. *Org Geochem* 30:1479–1493.
- Brignole, E.A. 1986. Supercritical fluid extraction. *Fluid Phase Equilibria* 29:133–144.
- Bringi, N.V. 1987. *Non-traditional Oil Seed and Oils of India*. Oxford/IBH, New Delhi.
- Caglar, A. 2003. Gaseous products from solid wastes. *Energy Edu Sci Technol* 10:107–110.

- Calvin, M. 1985. Fuel oils from higher plants. *Annu Proc Phytochem Soc Eur* 26:147–160.
- Chang, C.D., Silvestri, A.J. 1977. The conversion of methanol and other compounds to hydrocarbons over zeolite catalysts. *J Catal* 47:249–259.
- Chang, C.C., Wan, S.W. 1947. China's motor fuels from tung oil. *Ind Eng Chem* 39:1543–1548.
- Dandik, L., Aksoy, H.A. 1998. Pyrolysis of used sunflower oil in the presence of sodium carbonate by using fractionating pyrolysis reactor. *Fuel Process Technol* 57:81–92.
- Darnoko, D., Cheryan, M. 2000. Kinetics of palm oil transesterification in a batch reactor. *JAOCS* 77:1263–1267.
- Das, M., Das, S.K., Suthar, S.H. 2002. Composition of seed and characteristics of oil from Karingda [(*Citrullus lanatus* Thumb) Man of]. *Int J Food Sci Technol* 37:893–896.
- Demirbas, A. 1991a. Analysis of beech wood fatty acids by supercritical acetone extraction. *Wood Sci Technol* 25:365–370.
- Demirbas, A. 1991b. Fatty and resin acids recovered from spruce wood by supercritical acetone extraction. *Holzforschung* 45:337–339.
- Demirbas, A. 1998. Fuel properties and calculation of higher heating values of vegetable oils. *Fuel* 77:1117–1120.
- Demirbas, A. 2001. Mineral, protein, and fatty acids contents of hazelnut kernels. *Energy Edu Sci Technol* 7:37–43.
- Demirbas, A. 2002a. Biodiesel from vegetable oils via transesterification in supercritical methanol. *Energy Convers Mgmt* 43:2349–56.
- Demirbas, A. 2002b. Diesel fuel from vegetable oil via transesterification and soap pyrolysis. *Energy Sour* 24:835–841.
- Demirbas, A. 2003a. Chemical and fuel properties of seventeen vegetable oils. *Energy Sour* 25:721–728.
- Demirbas, A. 2003b. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. *Energy Convers Mgmt* 44:2093–2109.
- Demirbas, A. 2003c. Fuel conversional aspects of palm oil and sunflower oil. *Energy Sour* 25:457–466.
- Demirbas, A. 2004a. Recent advances in waste processing. *Energy Edu Sci Technol* 13:1–12.
- Demirbas, A. 2004b. Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons. *J Anal Appl Pyrol* 72:97–102.
- Demirbas, A. 2005. Pyrolysis of ground beech wood in irregular heating rate conditions. *J Anal Appl Pyrol* 73:39–43.
- Demirbas, A. 2006. Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics. *Energy Convers Mgmt* 47:2271–2282.
- Demirbas, A., Kara, H. 2006. New options for conversion of vegetable oils to alternative fuels. *Energy Sour Part A Recov Util Environ Effects* 28:619–626.
- Dry, M.E. 1981. The Fischer-Tropsch Synthesis. In: Anderson, J.R., Boudart, M. (eds.) *Catalysis-Science and Technology*, Vol. 1, Springer, New York, p. 160.
- Dykstra, G.J., Schwab, A.W., Selke, E., Sorenson, S.C., Pryde, E.H. 1988. Diesel fuel from thermal decomposition of soybean oil. *J Am Oil Chem Soc* 65:1781–1785.
- Eisenmenger, M., Dunford, N., Eller, F., Taylor, S. 2005. Pilot scale supercritical carbon dioxide extraction and characterization of wheat germ oil. *AOCS Proceedings*, Salt Lake City, UT.
- EPA (US Environmental Protection Agency), 2002. A comprehensive analysis of biodiesel impacts on exhaust emissions. Draft Technical Report, EPA420-P-02-001, October 2002.
- Erickson, D.R., Pryde, E.H., Brekke, O.L., Mounts, T.L., Falb, R.A. 1980. *Handbook of Soy Oil Processing and Utilization*. American Soybean Association and the American Oil Chemists Society. St. Louis, Missouri and Champaign, IL.
- Fang, T., Goto, M., Wang, X., Ding, X., Geng, J., Sasaki, M., Hirose, T. 2007. Separation of natural tocopherols from soybean oil byproduct with supercritical carbon dioxide. *J Supercrit Fluids* 40:50–58.
- Foidl, N., Foidl, G., Sanchez, M., Mittelbach, M., Hackel, S. 1996. *Jatropha curcas* L. As a source for the production of biofuel in nicaragua. *Bioresour Technol* 58:77–82.

- Fortes, I.C.P., Baugh, P.J. 1999. Study of analytical on-line pyrolysis of oils from macauba fruit (*Acrocomia sclerocarpa* M) via GC/MS. *J Braz Chem Soc* 10:469–477.
- Giannelos, P.N., Zannikos, F., Stournas, S., Lois, E., Anastopoulos, G. 2002. Tobacco seed oil as an alternative diesel fuel: physical and chemical properties. *Ind Crop Prod* 16:1–9.
- Goering, C.E. 1984. Final report for project on effect of nonpetroleum fuels on durability of direct- injection diesel engines under contract 59-2171-1-6-057-0, USDA, ARS, Peoria, IL.
- Goering, E., Schwab, W., Daugherty, J., Pryde, H., Heakin, J. 1982. Fuel properties of eleven vegetable oils. *Trans ASAE* 25, 1472–1483.
- Goodrich, J., Lawson, C., Lawson, V. P. 1980. *Kashaya Pomo Plants*. Heyday Books, Berkeley, CA.
- Gubitz, G. M., Mittelbach, M., Trabi, M. 1999. Exploitation of the tropical seed plant *Jatropha Curcas* L. *Bioresour Technol* 67:73–82.
- Gunstone, F.D., Hamilton, R.J. (eds.) 2001. *Oleochemicals manufacture and applications*. Sheffield Academic Press/CRC Press, Sheffield, UK/Boca Raton, FL.
- Haas, M.J., Cichowicz, D.J., Dierov, J.K. 2001. Lipolytic activity of California-laurel (*Umbellularia californica*). *J Am Oil Chem Soc* 78:1067–1071.
- He, H., Wang, T., Zhu, S. 2007. Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. *Fuel* 86:442–447.
- Hoyer, G.C. 1985. Extraction with supercritical fluids: Why, how, and so what? *Chetech J* 440–448.
- Islam, M. N., Islam, M.N., Beg, M.R.A. 2004. The fuel properties of pyrolysis liquid derived from urban solid wastes in Bangladesh. *Bioresour Technol* 92:181–186.
- Karaosmonoglu, F. 1999. Vegetable oil fuels: a review. *Energy Sour* 21:221–231.
- Karmee, S.K., Chadha, A. 2005. Preparation of biodiesel from crude oil of *Pongamia pinnata*. *Bioresour Technol* 96:1425–1429.
- Katikaneni, S.P.R., Adjaye, J.D., Bakhshi, N.N. 1995. Catalytic conversion of canola oil to fuels and chemicals over various cracking catalysts. *Can J Chem Eng* 73:484–497.
- Kekelidze, N.A. 1987. Essential oils of the bark and wood of the stems of *Laurus nobilis*. *Chem Nat Compounds* 23:384–385.
- Kerschbaum, S., Rinke, G. 2004. Measurement of the temperature dependent viscosity of biodiesel fuels. *Fuel* 83:287–291.
- Kilic, A., Altuntas, E. 2006. Wood and bark volatile compounds of *Laurus nobilis* L. *Holz als Roh-und Werkstoff* 64:317–320.
- Knothe, G., Krah, J., Van Gerpen, J. (eds.) 2005. *The Biodiesel Handbook*. AOCS Press, Champaign, IL.
- Knothe, G., Sharp, C.A., Ryan, T.W. 2006. Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine. *Energy Fuels* 20:403–408.
- Komers, K., Stloukal, R., Machek, J., Skopal, F. 2001. Biodiesel from rapeseed oil, methanol and KOH 3. Analysis of composition of actual reaction mixture. *Eur J Lipid Sci Technol* 103:363–3471.
- Leng, T.Y., Mohamed, A.R., Bhatia, S. 1999. Catalytic conversion of palm oil to fuels and chemicals. *Can J Chem Eng* 77:156–162.
- Lima, D.G., Soares, V.C.D., Ribeiro, E.B., Carvalho, D.A., Cardoso, E.C.V., Rassi, F.C., Mundim, K.C., Rubim, J.C., Suarez, P.A.Z. 2004. Diesel-like fuel obtained by pyrolysis of vegetable oils. *J Anal Appl Pyrol* 71:987–996.
- Ma, F., Hanna, M.A. 1999. Biodiesel production: a review. *Bioresour Technol* 70:1–15.
- Machacon, H.T.C., Matsumoto, Y., Ohkawara, C., Shiga, S., Karasawa, T., Nakamura, H. 2001. The effect of coconut oil and diesel fuel blends on diesel engine performance and exhaust emissions. *JSAE Rev* 22:349–355.
- Madras, G., Kolluru, C., Kumar, R. 2004. Synthesis of biodiesel in supercritical fluids. *Fuel* 83:2029–2033.
- Maschio, G., Koufopoulos, C., Lucchesi, A. 1992. Pyrolysis, a promising route for biomass utilization. *Bioresour Technol* 42:219–231.

- Meher, L.C., Kulkarni, M.G., Dalai, A.K., Naik, S.N. 2006a. Transesterification of karanja (*Pongamia pinnata*) oil by solid basic catalysts. *Eur J Lipid Sci Technol* 108:3898–397.
- Meher, L.C., Dharmagadda, V.S.S., Naik, S.N. 2006b. Optimization of alkali-catalyzed transesterification of *Pongamia pinnata* oil for production of biodiesel. *Bioresour Technol* 97:1392–1397.
- Mohan, D., Pittman, Jr., C.U., Steele, P.H. 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuels* 20:848–889.
- Mittelbach, M., Remschmidt, C. 2004. Biodiesels—The Comprehensive Handbook. Karl-Franzens University, Graz, Austria.
- Mittelbach, M., Gangl, S. 2001. Long storage stability of biodiesel made from rapeseed and used frying oil. *JAOCs* 78:573–577.
- Morrison, R.T., Boyd, R.N. 1983. Organic Chemistry, 4th edn. Allyn and Bacon, Singapore.
- Nagai, K., Seko, T. 2000. Trends of motor fuel quality in Japan. *JSAE Rev* 21:457–462.
- Nagel, N., Lemke, P. 1990. Production of methyl fuel from microalgae. *Appl Biochem Biotechnol* 24:355–361.
- Niehaus, R.A., Goering, C.E., Savage, Jr., L.D., Sorenson, S.C. 1986. Cracked soybean oil as a fuel for a diesel engine. *Trans ASAE* 29:683–689.
- Nitschke, W.R., Wilson, C.M. 1965. Rudolph Diesel, Pioneer of the Age of Power. The University of Oklahoma Press, Norman, OK.
- Paulaitis, M.E., Krukonis, V.J., Kurnik, R.T., Reid, R.C. 1983. Supercritical fluid extraction. *Rev Chem Eng* 1:181–248.
- Penninger, J.M.L., Radosz, M., McHugh, M.A., Krukonis, V.J. (eds.) 1985. Supercritical fluid technology. Elsevier, Amsterdam.
- Pioch, D., Lozano, P., Rasoanantoandro, M.C., Graille, J., Geneste, P., Guida, A. 1993. Biofuels from catalytic cracking of tropical vegetable oils. *Oleagineux* 48:289–291.
- Prakash, C.B. 1998. A critical review of biodiesel as a transportation fuel in Canada. A Technical Report. GCSI – Global Change Strategies International, Canada.
- Prins, M.J., Ptasiński, K.J., Janssen, F.J.J.G. 2004. Exergetic optimisation of a production process of Fischer–Tropsch fuels from biomass. *Fuel Process Technol* 86:375–389.
- Pryde, E.H., 1983. Vegetable oil as diesel fuel: overview. *JAOCs* 60:1557–1558.
- Pryor, R.W., Hanna, M.A., Schinstock, J.L., Bashford, L.L. 1982. Soybean oil fuel in a small diesel engine. *Trans ASAE* 26:333–338.
- Radovanovic, M., Venderbosch, R.H., Prins, W., van Swaaij, W.P.M. 2000. Some remarks on the viscosity measurement of pyrolysis liquids. *Biomass Bioenergy* 18:209–222.
- Rajaei, A., Barzegar, M., Yamini, Y. 2005. Supercritical fluid extraction of tea seed oil and its comparison with solvent extraction. *Eur Food Res Technol* 220:401–405.
- Ramachandra, T.V. 2004. Conversion of vegetable oils to alternative diesel-like fuels. *Energy Edu Sci Technol* 14:33–42.
- Ramadhas, A.S., Jayaraj, S., Muraleedharan, C. 2004. Biodiesel production from high FFA rubber seed oil. *Fuel* 84:335–340.
- Ramadhas, A.S., Jayaraj, S., Muraleedharan, C. 2004. Use of vegetable oils as I.C. engine fuels—a review. *Renew Energy* 29:727–742.
- S. Rapagnà, N. Jand and P. U. Foscolo
- Rapagnà, S., Jand, N., Foscolo, P.U. 1998. Catalytic gasification of biomass to produce hydrogen rich gas. *Int J Hydrogen Energy* 23:551–557.
- Reynolds, T., Dring, J.V., Hughes, C. 1991. Lauric acid-containing triglycerides in seeds of *Umbellularia californica* Nutt. (Lauraceae). *J Am Oil Chem Soc* 68:976–977.
- Roselius, W., Vitzthum, O., Hubert, P. 1975. Methods of production cocoa butter. US Patent 3,923,847.
- Sang, O.Y., Twaik, F., Zakaria, R., Mohamed, A., Bhatia, S. 2003. Biofuel production from catalytic cracking of palm oil. *Energy Sources* 25:859–869.
- Saucedo, E. 2001. Biodiesel. *Ingeniera Quimica* 20:19–29.
- Schelenk, H., Gellerman, J.L. 1960. Esterification of fatty acids with diazomethane on a small scale. *Anal Chem* 32:1412–1414.

- Schneider, G.M. 1978. Physicochemical principles of extraction with supercritical gases. *Agnew Chem Int Ed Eng* 17:716–727.
- Schwab, A.W., Bagby, M.O., Freedman, B. 1987. Preparation and properties of diesel fuels from vegetable oils. *Fuel* 66:1372–1378.
- Schwab, A.W., Dykstra, G.J., Selke, E., Sorenson, S.C., Pryde, E.H., 1988. Diesel fuel from thermal decomposition of soybean oil. *JAOCS* 65:1781–1786.
- Sensoz, S., Angin, D., Yorgun, S. 2000. Influence of particle size on the pyrolysis of rapeseed (*Brassica napus* L.): fuel properties of bio-oil. *Biomass Bioenergy* 19:271–279.
- Shay, E.G. 1993. Diesel fuel from vegetable oils: status and opportunities. *Biomass Bioenergy* 4:227–242.
- Sheehan, J., Cambreco, V., Duffield, J., Garboski, M., Shapouri, H., 1998. An overview of biodiesel and petroleum diesel life cycles. A report by US Department of Agriculture and Energy, Washington, D.C., pp.1–35.
- Schulz, H. 1999. Short history and present trends of FT synthesis. *Appl Catal A General* 186: 1–16
- Sie, S.T., Krishna, R. 1999. Fundamentals and selection of advanced FT-reactors. *Appl Catal A General* 186:55–70.
- Song, C. 2000. Introduction to chemistry of diesel fuels. In: Song, C., Hsu, C.S., Moshida, I. (eds.) *Chemistry of Diesel Fuels*. Taylor and Francis, London, p. 13.
- Sonntag, N.O.V. 1979. Reactions of fats and fatty acids. In: Swern, D. (ed.) *Bailey's Industrial Oil and Fat Products*, Vol. 1, 4th edn. Wiley, New York, p. 99.
- Srivastava and Prasad, R. 2000. Triglycerides-based diesel fuels. *Renew Sust Energy Rev* 4: 111–133
- Stelmachowski, M., Nowicki, L. 2003. Fuel from the synthesis gas—the role of process engineering. *Appl Energy* 74:85–93.
- Tijmensen, M.J.A., Faaij, A.P.C., Hamelinck, C.N., van Hardeveld, M.R.M. 2002. Exploration of the possibilities for production of Fischer Tropsch liquids and power via biomass gasification. *Biomass Bioenergy* 23:129–152.
- Voelker, T.A., Worrell, A.C., Anderson, L., Bleibaum, J., Fan, C., Hawkins, D.J., Radke, S.E., Davies, H.M. 1992. Fatty acid biosynthesis redirected to medium chains in transgenic oilseed plants. *Science* 257:72–74.
- Weisz, P.B., Haag, W.O., Rodeweld, P.G. 1979. Catalytic production of high-grade fuel (gasoline) from biomass compounds by shapedeactive catalysis. *Science* 206:57–58.
- Wikipedia. 2007. Neem oil characteristics. [http://en.wikipedia.org/wiki/Neem\\_oil](http://en.wikipedia.org/wiki/Neem_oil).
- Wright, H.J., Segur, J.B., Clark, H.V., Coburn, S.K., Langdom, E.E., DuPuis, R.N. 1944. A report on ester interchange. *Oil Soap* 21:145–148.
- Yarmo, M.A., Alimuniar, A., Ghani, R.A., Suliaman, A.R., Ghani, M., Omar, H., Malek, A. 1992. Transesterification products from the metathesis reaction of palm oil. *J Mol Catal* 76:373–379.
- Ziejewski, M., Kaufman, K.R., Schwab, A.W., Pryde, E.H. 1984. Diesel engine evaluation of a nonionic sunflower oil-aqueous ethanol microemulsion. *J Am Oil Chemists' Soc* 61: 1620–1626.
- Ziejewski, M., Goettler, H., Pratt, G.L. 1986. Paper No. 860301, International Congress and Exposition, Detroit, MI, 24–28 February 1986.
- Zhenyi, C., Xing, J., Shuyuan, L., Li, L. 2004. Thermodynamics calculation of the pyrolysis of vegetable oils. *Energy Sour* 26:849–856.